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# Materials Balance for Methyl Chloroform. Level II

JRB Associates, Inc.
McLean, VA

Prepared for

Environmental Protection Agency
Washington, DC

Jan 80

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# Materials Balance for Methyl Chloroform

## Level II

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A Level II materials balance for methyl chloroform was performed. Using 1978 data, the results of this materials balance included emission factors, the equations required to calculate environmental releases, and multimedia environmental losses for each production process and end use. Assumptions used to calculate the environmental losses were analyzed and an uncertainty was given to each. Recommendations were developed to close data gaps. These recommendations identified monitoring requirements and sites and suggested those end uses for future studies.

KEYWORDS: *Materials balance, *Environmental surveys, *Chloroform/methyl.

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# FINAL REPORT
# LEVEL II MATERIALS BALANCE
# METHYL CHLOROFORM

Prepared for:

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF PESTICIDES AND TOXIC SUBSTANCES
TASK NO. 3
Contract No. 68-01-5793
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THE FINAL REPORT PRESENTED HEREIN RESULTED FROM A LEVEL II MATERIALS BALANCE STUDY ON METHYL CHLOROFORM. THE RESULTS WERE BASED ON AN ANALYSIS OF ALL AVAILABLE INFORMATION RELEVANT TO THE MATERIALS BALANCE. UNCERTAINTIES AND FURTHER DATA REQUIREMENTS, INCLUDING SITE SAMPLING, ARE IDENTIFIED. THE GENERATION OF NEW DATA THROUGH MONITORING IS NOT WITHIN THE SCOPE OF THIS STUDY.

# MATERIALS BALANCE LEVELS

Materials balance studies are performed at three levels or depths of study and effort. In general the study of a chemical proceeds sequentially through these three levels. Particular chemicals are assigned to be studied at one of the levels on the basis of availability of information. The three levels are described below.

Level I:

A LEVEL I MATERIALS BALANCE requires the lowest level of effort and involves a survey of readily available information for constructing the materials balance. Ordinarily, many assumptions must be made in accounting for gaps in information; however, all are substantiated to the greatest degree possible. Where possible the uncertainties in numerical values are given, otherwise they are estimated. Data gaps are identified and recommendations are made for filling them. A Level I materials balance relies heavily on the EPA's Chemical Information Division as a source of data and references involving readily available information. Most Level I MB's are completed within a 3-6 week period; CID literature searches generally require a 2 week period to complete. Thus the total time required for completion of a Level I materials balance ranges from 5-7 weeks.

Level II:

A Level II MATERIALS BALANCE involves a greater level of effort, including an in-depth search for all information relevant to the materials balance. The search includes all literature, (concentrating on primary references), contacts with trade associations, other agencies, and industry to try to uncover unpublished information, and possibly site investigations. Uncertainties and further data needs are identified in the Level II report. Recommendations for site sampling needs for Level III are also identified.

Level III:

A Level III study requires generation of new data through monitoring and other means. It builds on the Level II literature searches and reviews of industrial production data by filling in data gaps through site visits and necessary monitoring. The data generated in this type of study are intended to be statistically valid and have known confidence values. The goal is a study upon which regulations or legal proceedings may be based.

# TABLE OF CONTENTS

Page

List of Tables v

List of Figures vii

Abstract ix

Executive Summary x

1.0 Introduction 1-1

2.0 Production of Methyl Chloroform 2-1

2.1 Global Production 2-6

2.2 Production of Methyl Chloroform from Vinyl Chloride 2-9

2.2.1 Production 2-9

2.2.2 Emissions to Air 2-10

2.2.3 Emissions to Water 2-22

2.2.4 Emissions to Air Due to Wastewater Treatment 2-24

2.2.5 Emissions to Land 2-26

2.2.6 Emissions to Air Due to the Incineration Disposal Method 2-27

2.2.7 Multimedia Environmental Losses 2-28

2.3 Production of Methyl Chloroform from Ethane 2-30

2.3.1 Production 2-30

2.3.2 Emissions to Air 2-32

2.3.3 Emissions to Water 2-38

2.3.4 Emissions to the Air Due to Wastewater Treatment 2-40

2.3.5 Emissions to Land 2-41

2.3.6 Emissions to the Air Due to the Incineration Disposal Method 2-42

2.3.7 Multimedia Environmental Losses 2-43

2.4 Vinylidene Chloride Process

2.4.1 Production 2-45

2.4.2 Emissions to Air 2-46

2.4.3 Emissions to Water 2-54

2.4.4 Emissions to Land 2-57

2.4.5 Multimedia Environmental Losses 2 58

Page

2.5 Indirect Production of Methyl Chloroform by Chlorination 2-60

2.6 Production of Methyl Chloroform from Natural Sources 2-63

2.7 Stockpiles 2-64

2.7.1 Introduction 2-64

2.7.2 Quantity Stockpiled 2-64

2.8 Imports 2-67

3.0 Uses and End Products 3-1

3.1 Metal Cleaning 3-2

3.1.1 Use of Methyl Chloroform in Metal Cleaning 3-2

3.1.2 Quantification of Methyl Chloroform Used in Metal Cleaning 3-2

3.1.3 Emissions from Cold Cleaning Operations 3-10

3.1.4 Emissions from Open Top Vapor Degreasers 3-18

3.1.5 Emissions from Conveyorized Vapor Degreasers 3-24

3.1.6 Emissions from Conveyorized Non-Boiling Degreasers 3-26

3.1.7 Multimedia Environmental Losses 3-27

3.2 Aerosol Products 3-30

3.2.1 Quantification of Methyl Chloroform Used in Aerosol Products 3-30

3.2.2 Use of Methyl Chloroform in Aerosol Products 3-30

3.2.3 Use and Emissions of Methyl Chloroform in Household Aerosol Products 3-31

3.2.4 Use and Emissions of Methyl Chloroform in Automotive Products 3-35

3.2.5 Use and Emissions of Methyl Chloroform in Coatings and Finishes 3-37

3.2.6 Use and Emissions of Methyl Chloroform in Personal Care Products and Pesticide Products 3-39

3.2.7 Multimedia Environmental Losses 3-41

3.3 Adhesives 3-43

3.3.1 Quantification of Methyl Chloroform Used in Adhesives 4-43

3.3.2 Use of Methyl Chloroform in the Adhesives Industry 3-44

3.3.3 Use and Emissions of Methyl Chloroform in Solvent Based Adhesives 3-47

3.3.4 Use and Emissions of Methyl Chloroform in Water Based Adhesives 3.57

3.3.5 Multimedia Environmental Losses 3-63

3.4 Textiles 3-65

3.4.1 Use and Quantification of Methyl Chloroform Used in Textiles 3-65

3.4.2 Emissions of Methyl Chloroform from the Production of Textiles 3-65

3.4.3 Multimedia Environmental Losses 3-75

3.5 Drain Cleaners and Septic Tank Cleaners 3-77

3.5.1 Use of Methyl Chloroform in Drain and Septic Tank Cleaners 3-77

3.5.2 Quantification of Methyl Chloroform Used in Drain and Septic Tank Cleaners 3-78

3.5.3 Multimedia Environmental Losses 3-80

3.6 Paints 3-86

3.6.1 Emissions to Air 3-86

3.6.2 Emissions to Water 3-87

3.6.3 Emissions to Land 3-88

3.6.4 Multimedia Environmental Losses 3-89

3.7 Inks 3-91

3.7.1 Emissions to Air 3-91

3.7.2 Emissions to Water and Land 3-92

3.7.3 Multimedia Environmental Losses 3-93

3.8 Miscellaneous Uses of Methyl Chloroform 3-95

3.8.1 Catalyst Preparation 3-96

3.8.2 Film Cleaning 3-97

3.8.3 Pharmaceuticals 3-101

3.8.4 Leather Tanning and Finishing 3-107

3.9 Exports 3-115

3.9.1 Exports of Methyl Chloroform 3-115

3.9.2 Method of Export 3-116

3.9.3 Trends in the Export of Methyl Chloroform 3-117

4.0 Disposal and Destruction of End-Products 4-1
  4.1 Contamination of End-Products 4-1
  4.2 Summary of Disposal/Destruction of End-Products 4-2
5.0 Summary of Environmental Releases of Methyl Chloroform 5-1
6.0 Summary of Uncertainties 6-1
7.0 Data Gaps and Recommendations 7-1
  7.1 Vinylidene Chloride Method 7-1
  7.2 Vinyl Chloride Process 7-2
  7.3 Ethane Process 7-3
  7.4 Metal Cleaning 7-4
  7.5 Aerosols 7-5
  7.6 Adhesives 7-6
  7.7 Textiles 7-7
  7.8 Paints 7-7
  7.9 Inks 7-8
  7.10 Septic Tank Cleaners and Drain Cleaners 7-8
  7.11 Catalyst Preparation 7-8
  7.12 Film Cleaning 7-9
  7.13 Leather Tanning 7-9

8.0 Discussion of National Academy of Science Study: STRATOSPHERIC OZONE DEPLETION BY HALOCARBONS

  8.1 Comparison of Production Estimates 8-1
  8.2 Discussion of Estimates for Ozone Depletion 8-3
References R-1

Appendices

  A - Process Description A-1
  B - Legislation Effecting the Use of Methyl Chloroform B-1
  C - Metal Cleaning C-1
  D - Products Containing Methyl Chloroform D-1
  E - Physical Properties of Methyl Chloroform E-1
  F - Breathing and Working Losses F-1

# LIST OF TABLES

| Table | | Page |
|---|---|---|
| 2.1-1 | Worldwide Production of Methyl Chloroform | 2-6 |
| 2.1-2 | Methyl Chloroform Production Capacity for Plants Outside the United States ($10^3$ kkg/year) | 2-7 |
| 2.2-1 | Selected Physical Properties of Vinyl Chloride, 1,1-Dichloroethane and Methyl Chloroform | 2-14 |
| 2.2-2 | Uncontrolled Emissions Due to Storage and Handling | 2-16 |
| 2.3-1 | Estimates of Total Uncontrolled VOC Emissions from a Model Plant Producing Methyl Chloroform from Ethane | 2-33 |
| 2.3-2 | Estimated Composition of Distillation Vent Gas from Model Plan Producing Methyl Chloroform from Ethane | 2-34 |
| 2.3-3 | Storage Tank Data for Methyl Chloroform (Ethane Feed) Model Plant | 2-37 |
| 2.5-1 | Concentrations of Volatile Chlorinated Organics Before and After Chlorination | 2-61 |
| 2.7-1 | Stockpiles of Methyl Chloroform | 2-66 |
| 3.1-1 | Estimates of Use of Methyl Chloroform in Solvent Degreasing | 3-5 |
| 3.1-2 | Major Control Variables for Cold Cleaners | 3-11 |
| 3.1-3 | Efficiencies of Control Options in Controlling Solvent Losses from Cold Cleaners | 3-12 |
| 3.1-4 | Control Variables - Open Top Vapor Degreasers | 3-20 |
| 3.3-1 | Adhesive Subcategories | 3-45 |
| 3.3-2 | Summary of Uncertainties for Environmental Release from Vessel Cleaning | 3-53 |
| 3.3-3 | Summary of Uncertainties for Environmental Releases from Vessel Cleaning | 3-61 |
| 3.4-1 | Subcategories of the Textile Industry | 3-67 |
| 3.9-1 | U. S. Export of Methyl Chloroform | 3-115 |
| 3.9-2 | U. S. Exports of Methyl Chloroform | 3-118 |
| 4.2-1 | Disposal and Destruction of End Products | 4-3 |
| 4.2-2 | Summary of Methyl Chloroform Landfilled Over 5 Year Period | 4-4 |
| 6.0-1 | Summary of Uncertainties | 6-2 |
| 8.1-1 | Estimated Global Production of Methyl Chloroform from 1977-1982 Using Three Possible Scenarios | 8-3 |

# TABLES

| Table | | Page |
|---|---|---|
| C-1 | Use of Solvent Degreasing Among Metal Working SIC Categories | C-1 |
| C-2 | Summary of Uncertainties for Waste Solvent | C-10 |
| C-3 | Summary of Uncertainties for Waste Solvent from Vapor Degreasing | C-17 |
| C-4 | Summary of Uncertainties for Waste Solvent from Conveyorized Vapor Degreasers | C-22 |
| C-5 | Summary of Uncertainties for Waste Solvent from Conveyorized Vapor Degreasers | C-28 |
| D-1 | List of Products Containing Methyl Chloroform | D-1 |
| D-2 | Registered Pesticides Containing Methyl Chloroform | D-3 |
| F-1 | Assumptions Used in Breathing and Working Loss Rate Calculations | F-2 |

## LIST OF FIGURES

| Figure | | Page |
|---|---|---|
| ES-1 | Summary of Materials Balance for Methyl Chloroform (1978) | xiii |
| 2.0-1 | Locations and Plant Capacities of the Production Plants of Methyl Chloroform | 2-2 |
| 2.0-2 | Location of Dow Chemical Company Methyl Chloroform Production Plant (Vinyl Chloride Process) | 2-3 |
| 2.0-3 | Location of PPG Industries, Inc. Methyl Chloroform Production Plant (Vinylidene Chloride Process) | 2-4 |
| 2.0-4 | Location of Vulcan Materials Company Methyl Chloroform Production Plant (Ethane Process) | 2-5 |
| 2.2-1 | Flow Diagram for Production of Methyl Chloroform from Vinyl Chloride | 2-12 |
| 2.2-2 | Multimedia Environmental Losses from the Vinyl Chloride-based Production Process | 2-29 |
| 2.3-1 | Flow Diagram for Production of Methyl Chloroform from the Ethane Process | 2-31 |
| 2.3-2 | Multimedia Environmental Losses from the Ethane-based Production Process | 2-44 |
| 2.4-1 | Derived Flow Diagram of the Production Process from Vinylidene Chloride | 2-47 |
| 2.4-2 | Multimedia Environmental Losses from the Vinylidene Chloride-based Production Process | 2-59 |
| 2.5-1 | The Haloform Reaction | 2-62 |
| 3.1-1 | Geographic Distribution of the Metalworking Industry | 3-3 |
| 3.1-2 | Overall Summary of Materials Balance for Methyl Chloroform in Metal Cleaning | 3-4 |
| 3.1-3 | Production Trends for Methyl Chloroform and Trichloroethylene | 3-8 |
| 3.1-4 | Points of Emission from a Cold Cleaning Operation | 3-10 |
| 3.1-5 | Multimedia Environmental Losses of Methyl Chloroform from Cold Cleaning | 3-14 |
| 3.1-6 | Geographic Distribution of Methyl Chloroform from Cold Cleaning Operations | 3-17 |
| 3.1-7 | Points of Emission from an Open Top Vapor Degreaser | 3-18 |
| 3.1-8 | Multimedia Environmental Losses of Methyl Chloroform from Open Top Vapor Degreaser | 3-21 |
| 3.1-9 | Geographic Distribution of Methyl Chloroform Losses from Vapor Degreasing | 3-25 |

Page

3.1-10 Multimedia Environmental Losses of Methyl Chloroform from Conveyorized Vapor Degreasers 3-24

3.1-11 Multimedia Environmental Losses from Methyl Chloroform from Conveyorized Nonboiling Degreasers 3-27

3.1-12 Overall multimedia Environmental losses for Methyl Chloroform from Metal Cleaning 3-28

3.2-1 Flow Diagram and Multimedia Environmental Losses of Methyl Chloroform from Aerosols 3-32

3.2-2 Multimedia Environmental Losses of Methyl Chloroform from the Production and Use of Aerosols 3-42

3.3-1 Geographic Distribution of Adhesive Industries 3-46

3.3-2 Multimedia Environmental Losses of Methyl Chloroform from Solvent Based Adhesives 3-56

3.3-3 Multimedia Environmental Losses of Methyl Chloroform from Water Based Adhesives 3-58

3.3-4 Total Multimedia Environmental Losses from the Formulation and Use of Adhesives 3-64

3.4-1 Flow Diagram of the Methyl Chloroform Used in Textiles 3-66

3.4-2 Multimedia Environmental Losses of Methyl Chloroform from Textiles 3-76

3.5-1 Multimedia Environmental Losses of Methyl Chloroform from Septic Tank Cleaners and Drain Cleaners 3-81

3.6-1 Multimedia Environmental Losses of Methyl Chloroform from Traffic Paints 3-90

3.7-1 Multimedia Environmental Losses of Methyl Chloroform from the Ink Industry 3-94

3.8-1 Multimedia Environmental Losses of Methyl Chloroform from Film Cleaning 3-100

3.8-2 Typical Process for Extraction of Medicinal Chemicals 3-103

3.8-3 Multimedia Environmental Losses of Methyl Chloroform from Pharmaceutical Processes 3-106

3.8-4 Flow Diagram for the Chrome Tanning Process 3-108

3.8-5 Flow Diagram for a Typical Leather Tanning Process 3-109

3.8-6 Multimedia Environmental Losses of Methyl Chloroform in the Tanning Industry 3-114

A-1 Flow Diagram for Methyl Chloroform from Vinyl Chloride A-3

A-2 Flow Diagram for Methyl Chloroform from Ethane A-7

A-3 Derived Flow Diagram of the Production Process from Vinylidene Chloride A-11

# ABSTRACT

A Level II materials balance for methyl chloroform was performed. Using 1978 data, the results of this materials balance included emission factors, the equations required to calculate environmental releases, and multimedia environmental losses for each production process and end use. Assumptions used to calculate the environmental losses were analyzed and an uncertainty was given to each.

Recommendations were developed to close data gaps. These recommendations identified monitoring requirements and sites and suggested those end uses for future studies.

This report was submitted in fulfillment of Contract Number 68-01-5793, Task No. 3 by JRB Associates, Inc. under the sponsorship of the United States Environmental Protection Agency.

# EXECUTIVE SUMMARY

This Level II materials balance reports emissions of methyl chloroform resulting from the production and use of this substance. A volatile organic compound, methyl chloroform is used primarily for metal cleaning (66 percent), as a vapor depressant in aerosols (7 percent), and for adhesive formulations requiring a solvent (7 percent). Methyl chloroform usage had been increasing steadily until 1976. Because of questions concerning its human health effects as a suspected carcinogen and its impact on the stratosphere, the Occupation Health and Safety Agency and the Environmental Protection Agency are considering placing restrictions on its use. These potential restrictions have inhibited the growth of methyl chloroform usage during the past few years.

The materials balance is presented for 1978 quantities of methyl chloroform. Estimates of environmental losses were derived using industry trends and information from industrial contacts and literature searches.

In 1978, an estimated 284,000 kkg of methyl chloroform were produced by three processes with different starting materials: vinyl chloride (Dow), ethane (Vulcan), and vinylidene chloride (PPG). These processes constitute 63 percent, 28 percent, and 9 percent respectively, of the total 1978 production. In 1979, PPG Industries, Inc. placed their vinylidene chloride process in reserve status and began producing methyl chloroform using vinyl chloride as the raw material. The releases to the environment from these production processes are discussed and calculated in Chapter 2 and summarized in Figure ES-1. Air emissions from various process vents, storage, handling, fugitive losses, aeration during waste water treatment, and the incineration of heavy-end wastes were estimated to be 176 kkg. Effluent emissions from the production of methyl chloroform totaled 0.29 kkg for 1978. Emissions to land from these processes were 0.004 kkg.

Quantities produced, but not sold were assumed to be placed in stockpiles. Stockpiles represented 17,500 kkg or approximately 6.2 percent

of total production in 1978. Emissions from stockpiles were included in the total emissions from product storage.

Imports of methyl chloroform were not identified during our literature search nor were any suggested during phone conversations with industry sources. Our analysis found no sources of natural or indirect production.

The quantity of methyl chloroform exported in 1978 was 18,000 kkg (6.3 percent of total production). Table 3.9-1 lists the quantities exported to foreign countries.

There were no consumptive uses of methyl chloroform in 1978. Methyl chloroform had been used by Dow to produce vinylidene chloride but this process was terminated in 1974. Secondary contamination of other products was not found and is considered unlikely.

Nonconsumptive uses (and the approximate percentage of methyl chloroform production used by each) were: metal cleaning (66.1 percent), aerosols (7.0 percent), adhesives (7.0 percent), textiles (1.0 percent), paints (1.8 percent), inks (1.0 percent), drain cleaners (0.5 percent), film cleaning (0.1 percent), pharmaceuticals (0.1 percent), leather tanning (0.1 percent) and other unspecified miscellaneous uses (2.8 percent) (primarily miscellaneous solvent-cleaning applications). Emissions from each nonconsumptive use are identified in Figure ES-1.

Metal cleaning was the primary end use of methyl chloroform and also the primary source of emissions. Emissions to air, land, and water from metal cleaning operations totaled 159,500, 22,200, and 975 kkg respectively. Air emissions resulting from metal cleaning represent almost 75 percent of the total air emissions for all sources. Water and solid waste emissions from metal cleaning are greater than 40 and 84 percent, respectively, of the total emissions in these categories.

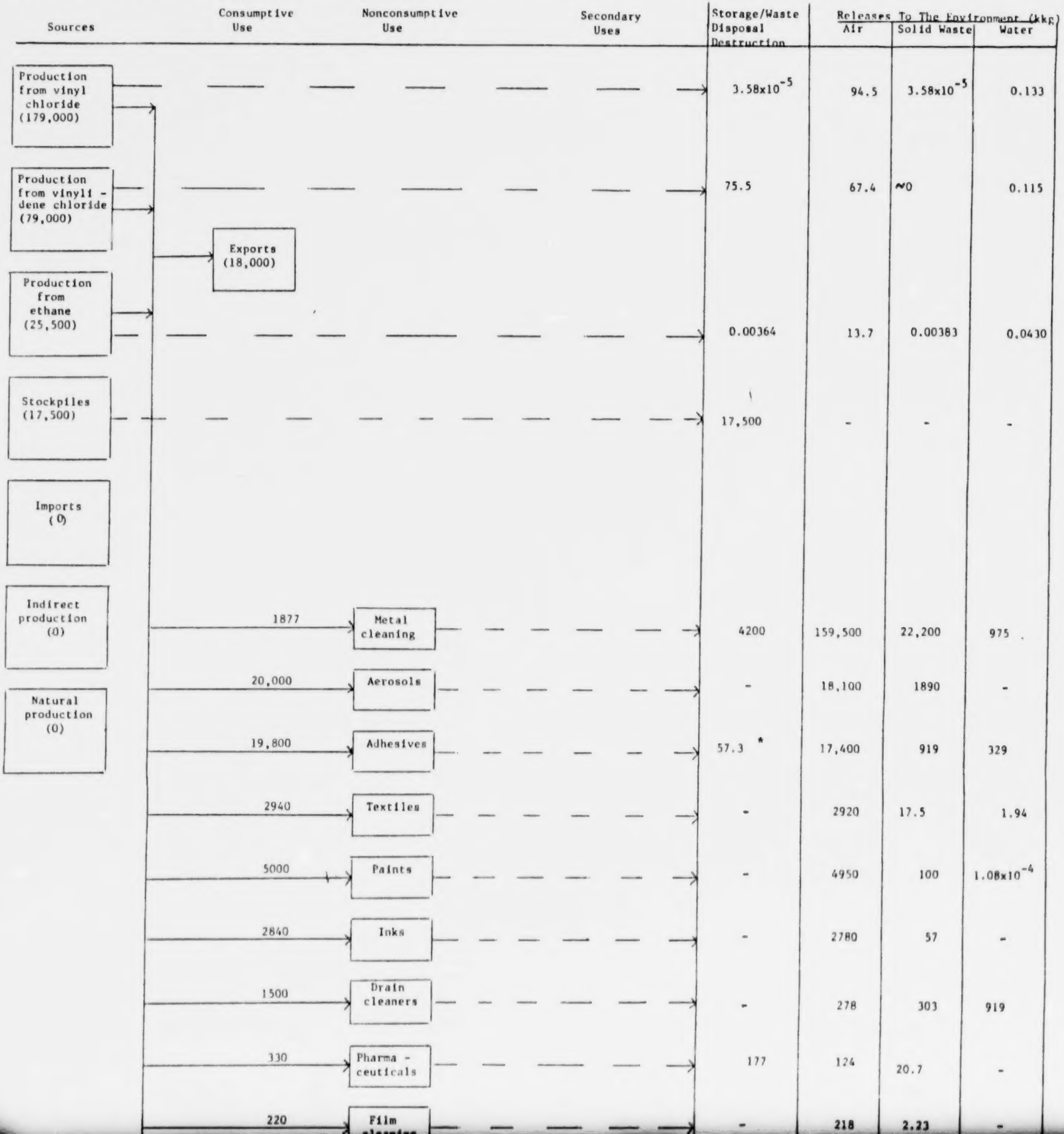
Two major uses, adhesives and aerosols, each account for approximately 7 percent of the annual production of methyl chloroform. Air emissions from these uses were nearly identical (17,400 and 18,100 kkg) but solid waste and water emissions differed significantly. For adhesives, 919 kkg were lost through solid waste and 329 kkg in water effluent. For aerosols, almost 1900 kkg were lost in solid wastes, yet because of the formulation process and end use, no quantifiable amount of methyl chloroform was released to waste waters.

Total emissions from nonconsumptive uses were 213,000 kkg to the air, 26,200 kkg in solid wastes, and 2,400 kkg in water effluent.

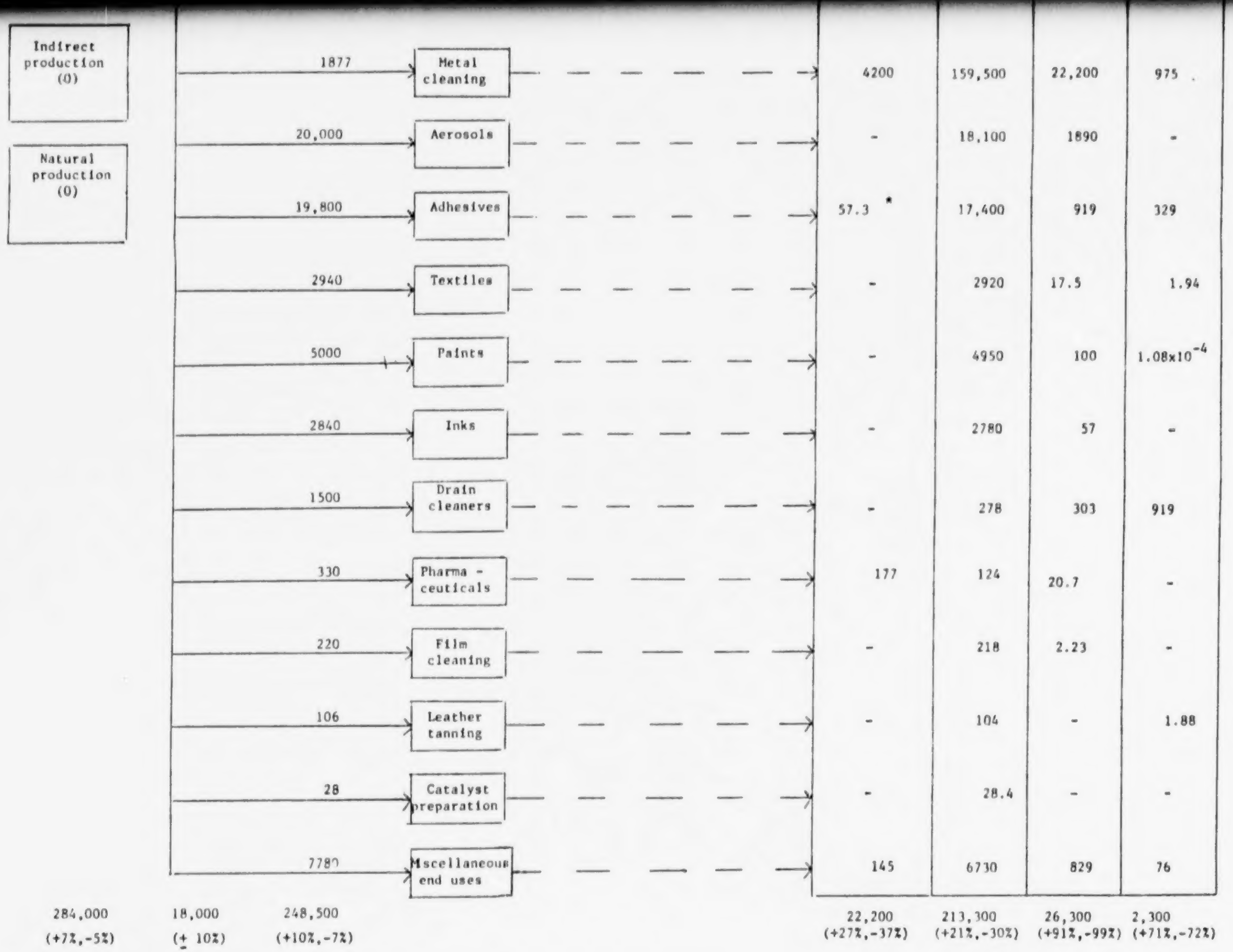
Waste disposal and destruction accounted for 4,700 kkg of the total methyl chloroform produced. Metal cleaning was the largest source of methyl chloroform landfilled or incinerated (4,200 kkg or 91 percent of the total). Of the production processes, waste disposal and destruction for vinylidene chloride were proportionately higher than for the other two processes. This is due to the greater level of control technology assumed for this process.

This report contains many estimates, including some for important numbers. The quantities of methyl chloroform in minor end uses will be required for meaningful emissions estimates. Data gaps are identified in Chapter 7, which also gives our recommendations for filling them.

## ES-1 Summary of Materials Balance for Methyl Chloroform (1978)



| Sources | Consumptive Use | Nonconsumptive Use | Secondary Uses | Storage/Waste Disposal Destruction | Releases To The Environment (kkg) Air | Solid Waste | Water |
|---|---|---|---|---|---|---|---|
| Production from vinyl chloride (179,000) | | | | $3.58 \times 10^{-5}$ | 94.5 | $3.58 \times 10^{-5}$ | 0.133 |
| Production from vinylidene chloride (79,000) | | | | 75.5 | 67.4 | ~0 | 0.115 |
| | Exports (18,000) | | | | | | |
| Production from ethane (25,500) | | | | 0.00364 | 13.7 | 0.00383 | 0.0430 |
| Stockpiles (17,500) | | | | 17,500 | - | - | - |
| Imports (0) | | | | | | | |
| Indirect production (0) | | | | | | | |
| Natural production (0) | | | | | | | |
| | 1877 | Metal cleaning | | 4200 | 159,500 | 22,200 | 975 |
| | 20,000 | Aerosols | | - | 18,100 | 1890 | - |
| | 19,800 | Adhesives | | 57.3 * | 17,400 | 919 | 329 |
| | 2940 | Textiles | | - | 2920 | 17.5 | 1.94 |
| | 5000 | Paints | | - | 4950 | 100 | $1.08 \times 10^{-4}$ |
| | 2840 | Inks | | - | 2780 | 57 | - |
| | 1500 | Drain cleaners | | - | 278 | 303 | 919 |
| | 330 | Pharmaceuticals | | 177 | 124 | 20.7 | - |
| | 220 | Film | | - | 218 | 2.23 | - |


Indirect production (0)
Natural production (0)
1877
Metal cleaning
4200
159,500
22,200
975
20,000
Aerosols
-
18,100
1890
-
19,800
Adhesives
57.3 *
17,400
919
329
2940
Textiles
-
2920
17.5
1.94
5000
Paints
-
4950
100
1.08x10^-4
2840
Inks
-
2780
57
-
1500
Drain cleaners
-
278
303
919
330
Pharma - ceuticals
177
124
20.7
-
220
Film cleaning
-
218
2.23
-
106
Leather tanning
-
104
-
1.88
28
Catalyst preparation
-
28.4
-
-
7780
Miscellaneous end uses
145
6730
829
76
284,000 (+7%,-5%)
18,000 (± 10%)
248,500 (+10%,-7%)
22,200 (+27%,-37%)
213,300 (+21%,-30%)
26,300 (+91%,-99%)
2,300 (+71%,-72%)

[*] 1017 kkg of Methyl Chloroform used in adhesives are reclaimed and sold as waste solvent

# 1.0 INTRODUCTION

This report was prepared in response to a task order from the U.S. Environmental Protection Agency (EPA) for a Level II materials balance study on methyl chloroform. The study is primarily concerned with the flow and releases of methyl chloroform from its production to its end uses.

In order to provide EPA a material balance report on methyl chloroform, available information was thoroughly and carefully analyzed. In most cases where changes in recent years have made published data obsolete, industrial sources were contacted to obtain updated information. Thus, the results generated in this report are more applicable to a Level II than to a Level I materials balance. In some cases where data could not be obtained, estimates were provided based on available information on similar processes.

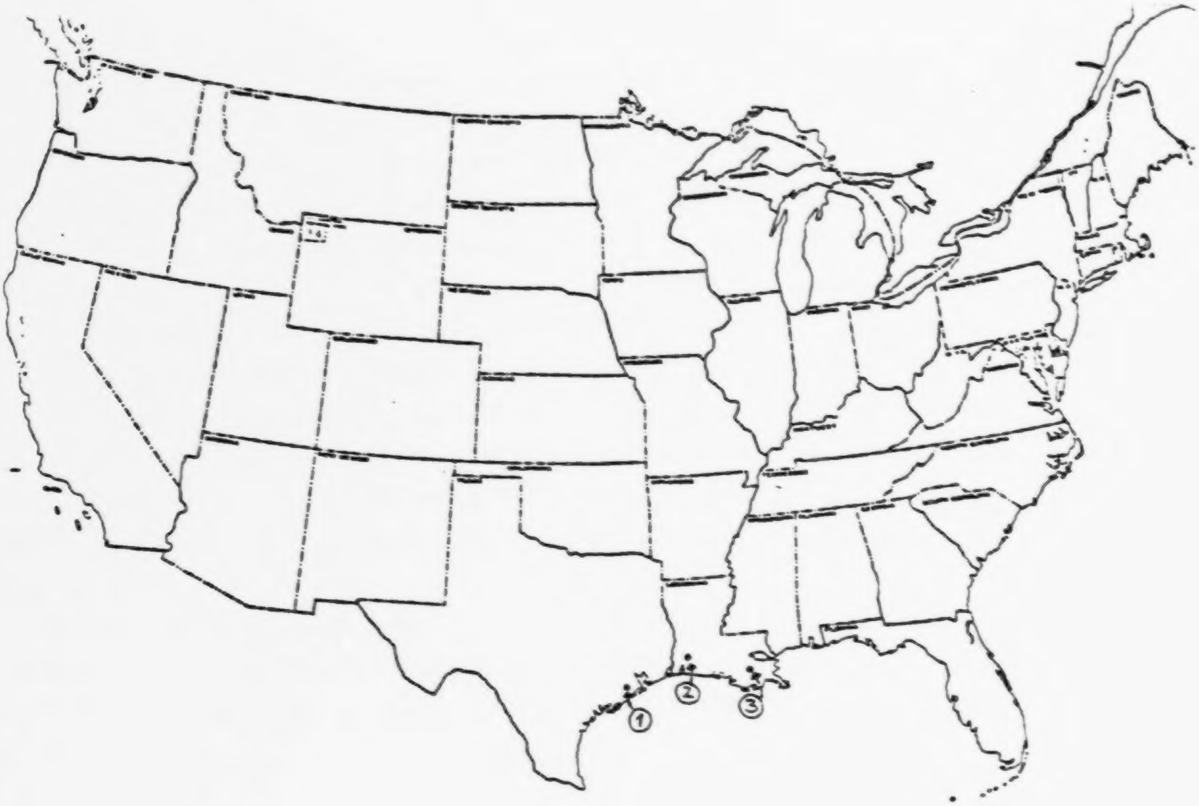
This study also presents an analysis of the National Academy of Sciences (NAS) report on methyl chloroform in the stratosphere. Since methyl chloroform has been identified as an ozone-depleting agent, a comparison of the results of our study with the Academy's has been provided. The differences between the reports with respect to the future stratospheric impact of methyl chloroform are highlighted.

This report contains numerous calculations resulting in numbers that are not directly additive. These values are the result of always rounding to three (3) significant figures.

# 2.0 PRODUCTION OF METHYL CHLOROFORM

The quantity of methyl chloroform produced in 1978 was reported as 284,000 kkg (+7%, -5%) (USITC, 1978). This figure is based on the amount of product reported to the International Trade Commission by eech producer. The upper and lower bounds presented in Sections 2.2.1, 2.3.1 and 2.4.1 form the basis for the uncertainty of the overall production figure. Methyl chloroform was reported to be produced by 3 different methods: a) the vinyl chloride method, b) the ethane method and c) the vinylidene chloride method. The percentages of methyl chloroform produced by each method are, respectively, 63 percent, 9 percent, and 28 percent. The following sections will present an in-depth discussion of each process. Figures 2.0-1 - 2.0-4 shows the locations of methyl chloroform production sites in the United States.

Natural production sources have not been identified and indirect sources, such as chlorination of public water, were not found to contribute significantly ( $<$.001 per cent) to the total production.



| Name and Location<br>Production Plant | 1978<br>Plant Capacity<br>(kkg) | 1979<br>Plant Capacity<br>(kkg) |
|---|---|---|
| Dow Chemical Co., Freeport TX | 204,000 | 340,000 |
| PPG Industries Inc., Lake Charles LA | 136,000 | 136,000 |
| Vulcan Materials Co., Geismar LA | 29,500 | 93,000 |

Figure 2.0-1 Locations and Plant Capacities of the Production Plants of Methyl Chloroform

Source: EPA, 1979a

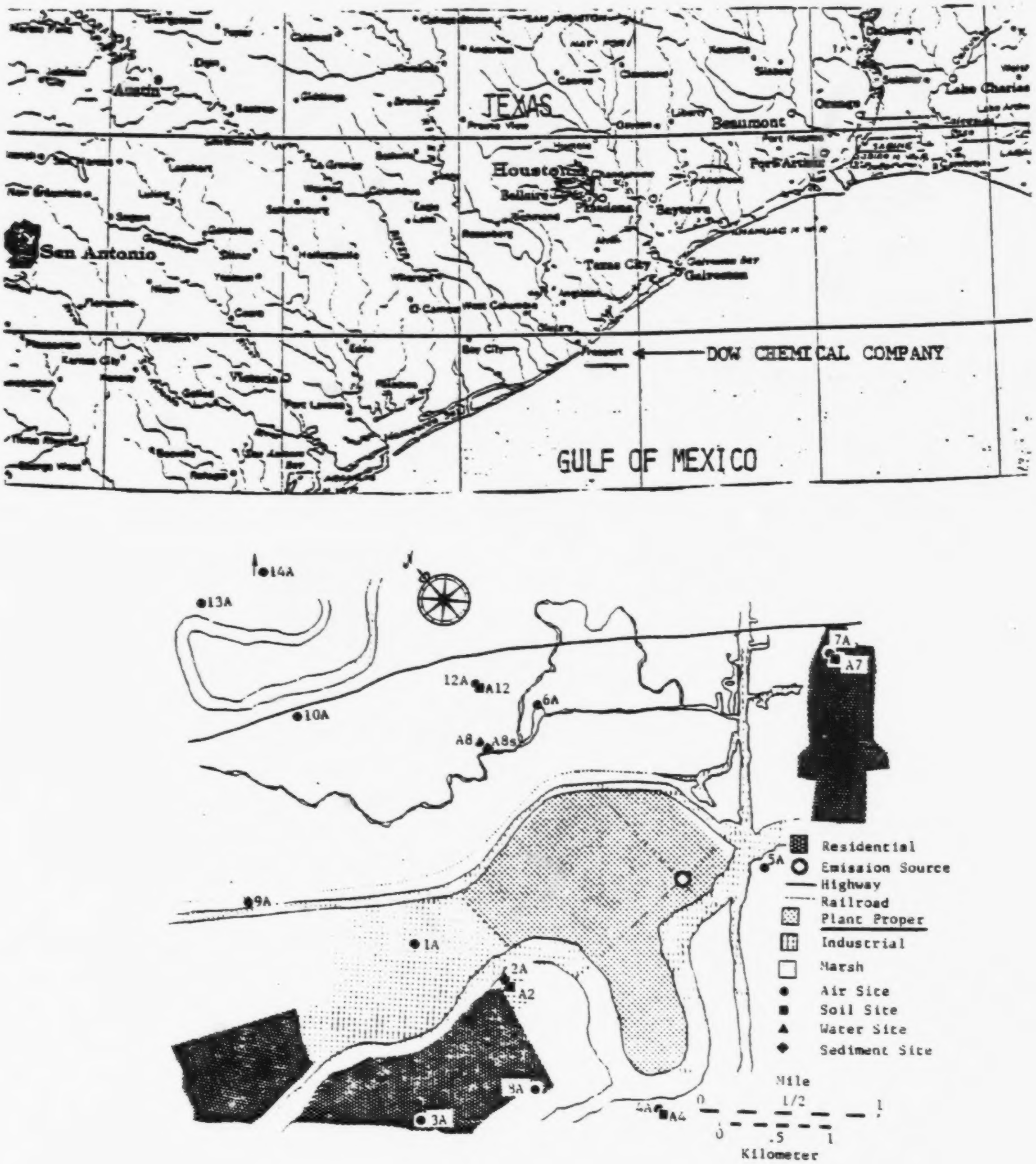

TEXAS
Austin
San Antonio
Houston
Bellaire
Pasadena
Baytown
Beaumont
Orange
Port Arthur
Lake Charles
Texas City
Galveston
Bay City
Victoria
Freeport
DOW CHEMICAL COMPANY
GULF OF MEXICO
14A
13A
10A
12A
A12
6A
A8
A8s
7A
A7
9A
1A
2A
A2
3A
3A
4A
A4
5A
Residential
Emission Source
Highway
Railroad
Plant Proper
Industrial
Marsh
Air Site
Soil Site
Water Site
Sediment Site
Mile
0
1/2
1
0
.5
1
Kilometer

Figure 2.0-2 Location of Dow Chemical Company Methyl Chloroform Production Plant (Vinyl Chloride Process)

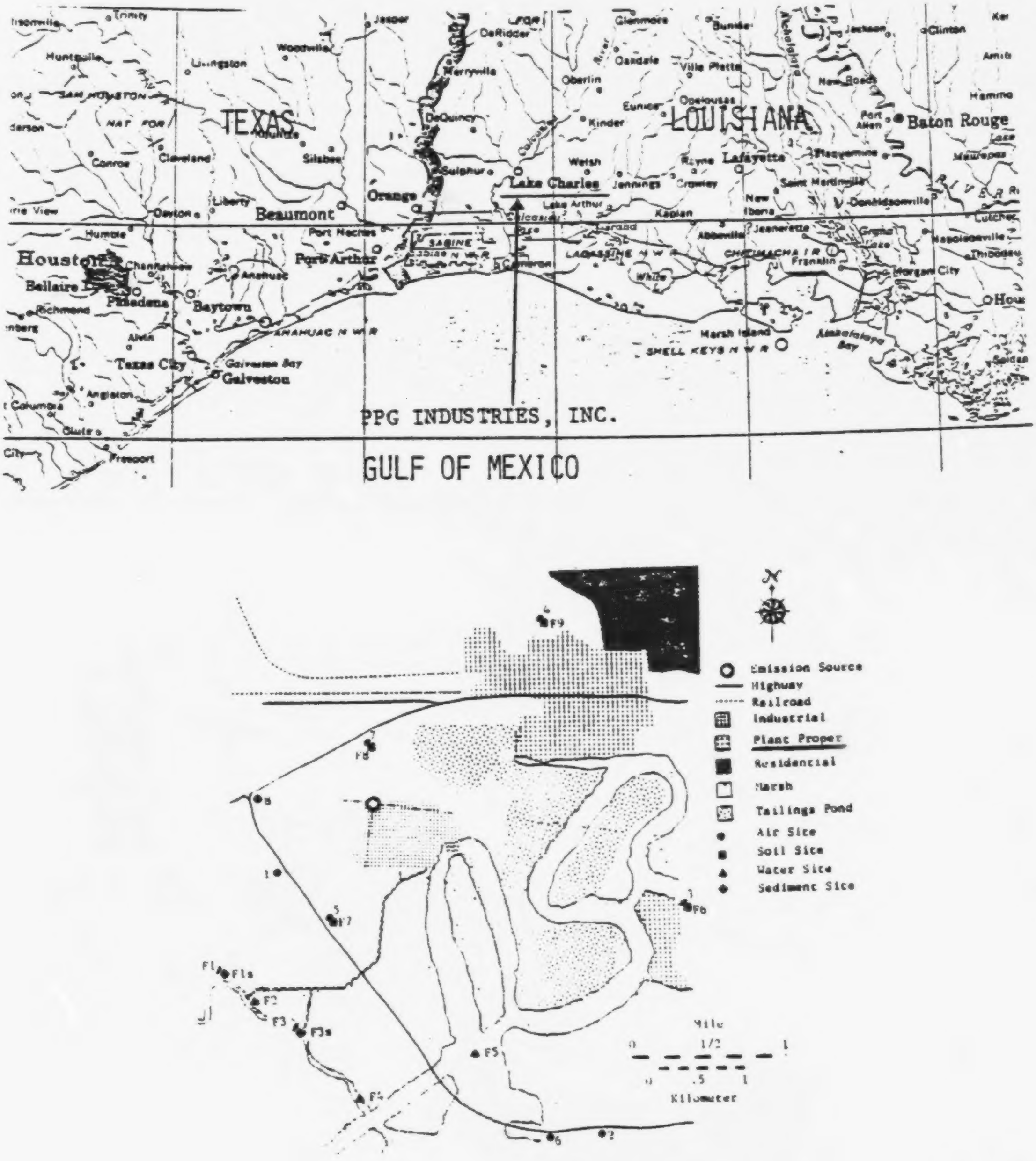

TEXAS
LOUISIANA
Houston
Bellaire
Pasadena
Baytown
Texas City
Galveston
Beaumont
Port Arthur
Orange
Lake Charles
Lafayette
Baton Rouge
Morgan City
PPG INDUSTRIES, INC.
GULF OF MEXICO
N
Emission Source
Highway
Railroad
Industrial
Plant Proper
Residential
Marsh
Tailings Pond
Air Site
Soil Site
Water Site
Sediment Site
Mile
0
1/2
1
0
.5
1
Kilometer
F1
F1a
F2
F3
F3a
F4
F5
F6
F7
F8
F9

Figure 2.0-3 Location of PPG Industries, Inc. Methyl Chloroform Production Plant (Vinylidene Chloride Process)

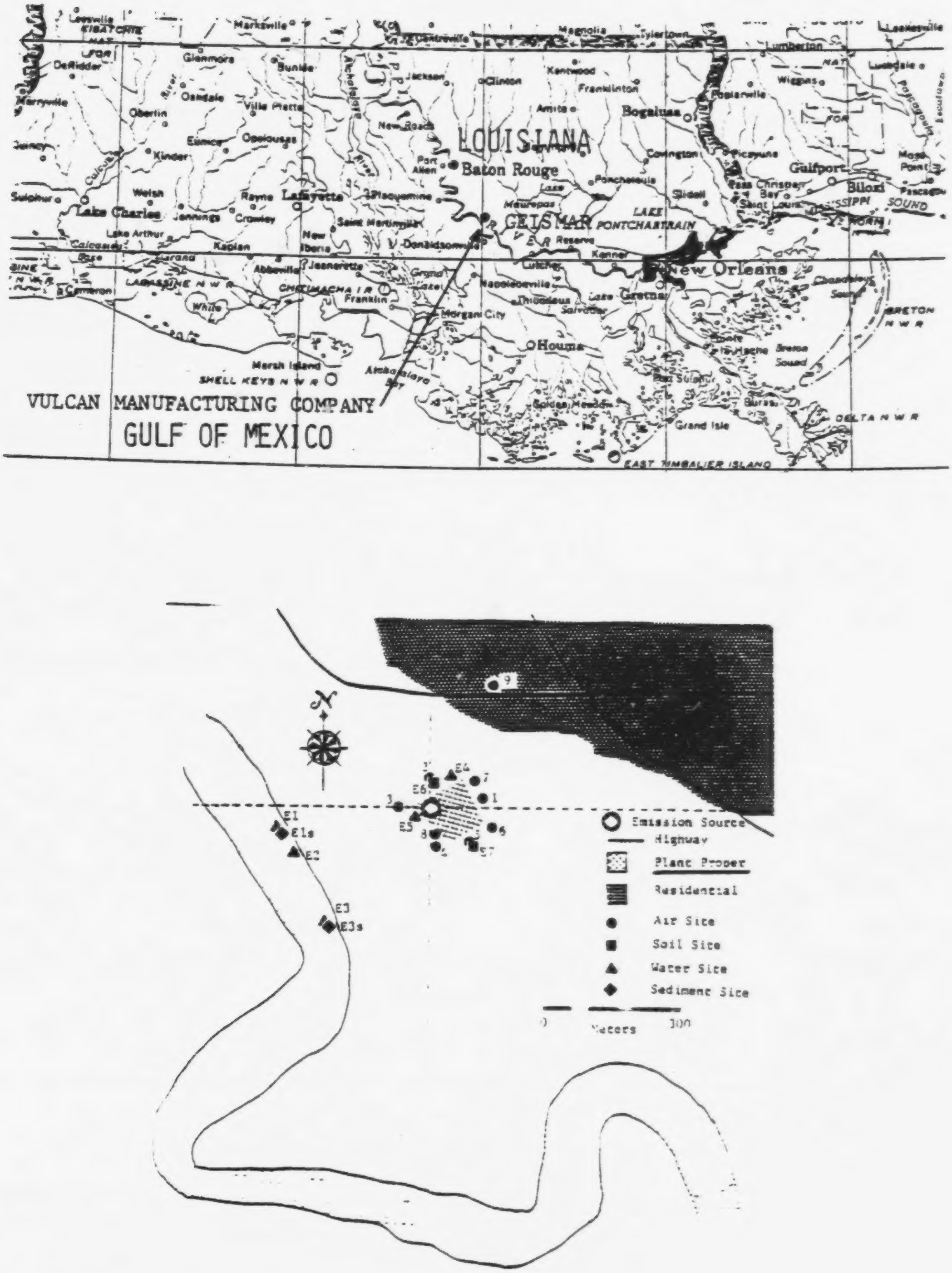

LOUISIANA
Baton Rouge
GEISMAR
LAKE PONTCHARTRAIN
New Orleans
Lafayette
Lake Charles
Bogalusa
Gulfport
Biloxi
Houma
Morgan City
Thibodaux
Donaldsonville
Plaquemine
New Iberia
VULCAN MANUFACTURING COMPANY
GULF OF MEXICO
9
3
E4
7
E6
1
E5
6
8
4
E7
E1
E1s
E2
E3
E3s
Emission Source
Highway
Plant Proper
Residential
Air Site
Soil Site
Water Site
Sediment Site
0
Meters
300

Figure 2.0-4 Location of Vulcan Materials Company Methyl Chloroform Production Plant (Ethane Process)

## 2.1 GLOBAL PRODUCTION

Table 2.1-1 shows worldwide emissions of methyl chloroform from 1974-1978. These estimates were made by the Corporate Product Department of Dow Chemical (Neely and Agin, 1978) and exclude any methyl chloroform produced in the Soviet Union and other Iron Curtain countries. As judged from a previous Dow publication (Neely and Plonka, 1978), total worldwide production may be about 3 to 6 percent greater than total annual emissions.

Table 2.1-1 Worldwide Production of Methyl Chloroform(1)

| Year | Global Releases[2] ($10^3$ kkg) | U.S. Production[3] [4] ($10^3$ kkg) | Production Outside U.S. ($10^3$ kkg) | U.S. Production as a Percent of Global Releases |
|---|---|---|---|---|
| 1974 | 363 | 268 | 95 | 74 |
| 1975 | 365 | 208 | 157 | 60 |
| 1976 | 416 | 261 | 155 | 63 |
| 1977 | 427 | 287 | 140 | 67 |
| 1978 | 477 | 284 | 194 | 59 |

[1] USSR and Iron Curtain Countries not included.

[2] Neely and Agin, 1978. These figures represent emissions rather than production; production may be 3 to 6 percent higher than total emissions.

[3] U.S. Tariff Commission, 1978

[4] EPA, 1979a.

Table 2.1-1 indicates that production of methyl chloroform is increasing less rapidly in the United States than in other countries. Although still producing more than half of the world supply, the United States contributes a signficiantly smaller percentage than it did in the early 1970's.

The capacities of several foreign plants for which information was available are listed in Table 2.1-2.

Table 2.1-2 -- Methyl Chloroform Production Capacity for Plants Outside the United States ($10^3$ kkg/year)

| Country | 1971 | 1975 | 1977 | 1979 | Source |
|---|---|---|---|---|---|
| Japan - Tao Gosei | 18 | 18 | 18 | 36 | PROMPT, 1979 |
| Central Kagaku | 6 | 6 | 6 | 6 | PROMPT, 1979 |
| Kanto Denka | 12 | 12 | 12 | 12 | PROMPT, 1979 |
| Toya Sada | 12 | 12 | 12 | 12 | PROMPT, 1979 |
| Asahi-Dow |  | 40 | 40 | 40 | PROMPT, 1979 |
| Ashi-Penn |  |  |  | 20 | PROMPT, 1979 |
| Mitsubishi |  |  |  | 160 | McCracken, 1979 |
| Europe - Dow |  |  | 180 | 180 | McCracken, 1979 |
| England |  |  |  | 150[1] | McCracken, 1979 |

[1] This plant is proposed but will not necessarily be on line by 1979.

This list is evidently not inclusive: Table 2.1-1 indicates that 1975 production outside the United States was 157,000 kkg, but plant capacities listed in Table 2.1-2 account for only 88,000 kkg or

56 percent of the total produced outside the United States. The large increase in production outside the United States between 1977 and 1978 is probably attributable to the Dow-Europe plant.

Table 2.1-1 shows that total global releases for 1978 increased by 13 percent, while U.S. production remained stable. Foreign production increased from 140,000 kkg in 1977 to 194,000 kkg in 1978, a 33 percent increase in one year. Although production of 194,000 kkg of methyl chloroform is within the known capacity of foreign plants (Table 2.1-2), it is unlikely that European market conditions could create such a significant increase in demand. Thus, it is evident that the 1979 global releases suggested by Neely and Agin are overestimated.

To improve the accuracy of global production figures for methyl chloroform, information will be required from foreign countries with production facilities.

## 2.2 PRODUCTION OF METHYL CHLOROFORM FROM VINYL CHLORIDE

### 2.2.1 Production

Methyl chloroform (1,1,1-trichloroethane) can be produced by the vinyl chloride method. The main reactions involved in this process include the hydrochlorination of vinyl chloride into 1,1-dichloroethane in the presence of a catalyst and then the chlorination of 1,1-dichloroethane into methyl chloroform. The chemical reactions are presented below (Hydroscience, 1979):

$$\underset{\substack{\text{Vinyl}\\\text{Chloride}}}{CH_2 = CHCl} \quad + \underset{\substack{\text{Hydrogen}\\\text{Chloride}}}{HCl} \quad + \quad \xrightarrow[\text{Catalyst}]{Fe\ Cl_3} \quad \underset{\text{1,1-dichloroethane}}{CH_3 - CHCl_2}$$

$$\underset{\text{1,1-dichloroethane}}{CH_3 - CHCl_2} \quad + \quad \underset{\text{Chlorine}}{Cl_2} \longrightarrow \underset{\text{Methyl Chloroform}}{CH_3 - CCl_3}$$

An average yield rate of 98 percent is achieved with this method (EPA 1979a; Mannsville Chemical Products, 1978). Unconverted materials are either recycled within the process, used as raw materials in other processes, or wasted. A more detailed discussion of this process is presented in Appendix A.

According to MRI (EPA, 1979a), the Dow Chemical Company produced 181,000 kkg of methyl chloroform in 1976 using vinyl chloride as a raw material. This represented approximately 63 percent of the total U.S. production quantity, but one percent below 1975. The methyl chloroform plant capacity of Dow also represented 63 percent of the total in 1976. By 1979 though, Dow accounted for less than 60 percent of the plant capacity due to extensive plant expansion by their competitors, Vulcan and PPG (EPA, 1979a).

Assuming that the percentage of Dow's market capture remained steady, we estimate the 1978 market share to be 63 percent. Therefore, the 1978 Dow methyl chloroform production can be estimated as follows:

$$\begin{array}{ccccc} \text{Production from} & & \text{1978 Total U.S.} & & \text{Percent Market} \\ \text{Vinyl Chloride} & = & \text{Production of} & \times & \text{Capture of} \\ \text{Method} & & \text{Methyl Chloroform} & & \text{Process} \\ & & & & \\ 179{,}000 \text{ kkg} & = & (284{,}000 \text{ kkg}) & & (0.63) \end{array}$$

The uncertainty of this number is +6% and -7%. The upper bound assumes the Dow market share is equivalent to its percentage (65.2 percent) of total U.S. methyl chloroform production capacity prior to plant expansion by all three producers (EPA, 1979a). The lower bound assumes the Dow market share is equivalent to its percentage (59.8 percent) of the total U.S. 1979 methyl chloroform production capacity after all three producers had completed their proposed plant expansions (EPA, 1979a). The confidence placed on the estimated Dow production for 1978 is primarily due to the consistency of the various market shares reported by MRI covering the previous 10 years (EPA, 1979a).

Prior to 1977, Dow Chemical Company and the Ethyl Corporation produced methyl chloroform using vinyl chloride as the raw material. During 1976, Ethyl ceased the production of methyl chloroform (EPA, 1979a). In September 1979, Vulcan Materials Company began operating a new methyl chloroform production facility. The new facility, using vinyl chloride as the raw material, will become Vulcan's primary source of methyl chloroform production. Since all calculations here are being performed with 1978 data, methyl chloroform produced from vinyl chloride at the Vulcan facility will not be included. The equations presented below will enable readers to estimate emissions from the Vulcan facility using future data.

### 2.2.2 Emissions to Air

Storage vents, handling and fugitive losses were identified as the most significant locations for methyl chloroform air releases.

Secondary sources of air emissions included wastewater treatment and the incineration of residues (Hydroscience, 1979).

Figure 2.2-1 represents the flow diagram for the production of methyl chloroform from vinyl chloride. A discussion of the losses using this flow diagram is presented in the following sections.

### 2.2.2.1 Emissions to Air From the Light Ends Column (Vent $A_1$)

According to MRI and TRW, "trichloroethane" is emitted to the air during the production of methyl chloroform from vinyl chloride (EPA, 1979a; TRW, 1975). The configuration of the "trichloroethane", either 1,1,1-trichloroethane (methyl chloroform) or 1,1,2-trichloroethane, was not identified. These emissions were identified in the hydrochlorination reactor vent gases. However, Hydroscience did not suggest that any methyl chloroform emissions were released from this reactor or columns associated with the reactor.

Since the TRW and MRI reports disagree with the emissions estimated by Hydroscience, an analysis of the hydrochlorination reactor, heavy ends column and light ends column was performed.

If the quantities of methyl chloroform (or "trichloroethane") and 1,1-dichloroethane were present in the vent gases as proposed by MRI and TRW (0.009 kkg methyl chloroform/kkg and 0.0085 kkg dichloroethane/kkg of methyl chloroform produced), then the hydrochlorination reactor would have to produce approximately a 50-50 mixture of the two organic compounds (EPA, 1979a; TRW, 1975). However, the hydrochlorination process is known to convert vinyl chloride to 1,1-dichloroethane at an efficiency greater than 98 percent (EPA, 1979a; Mannsville Chemical Products, 1978). Therefore, it is highly improbable that methyl chloroform releases could be so high.

Assuming that methyl chloroform (MC) and dichloroethane (DCE) were measured in the vent gases at a ratio of 9:8.5, the percentage of methyl chloroform formulated by hydrochlorination can be calculated as follows:

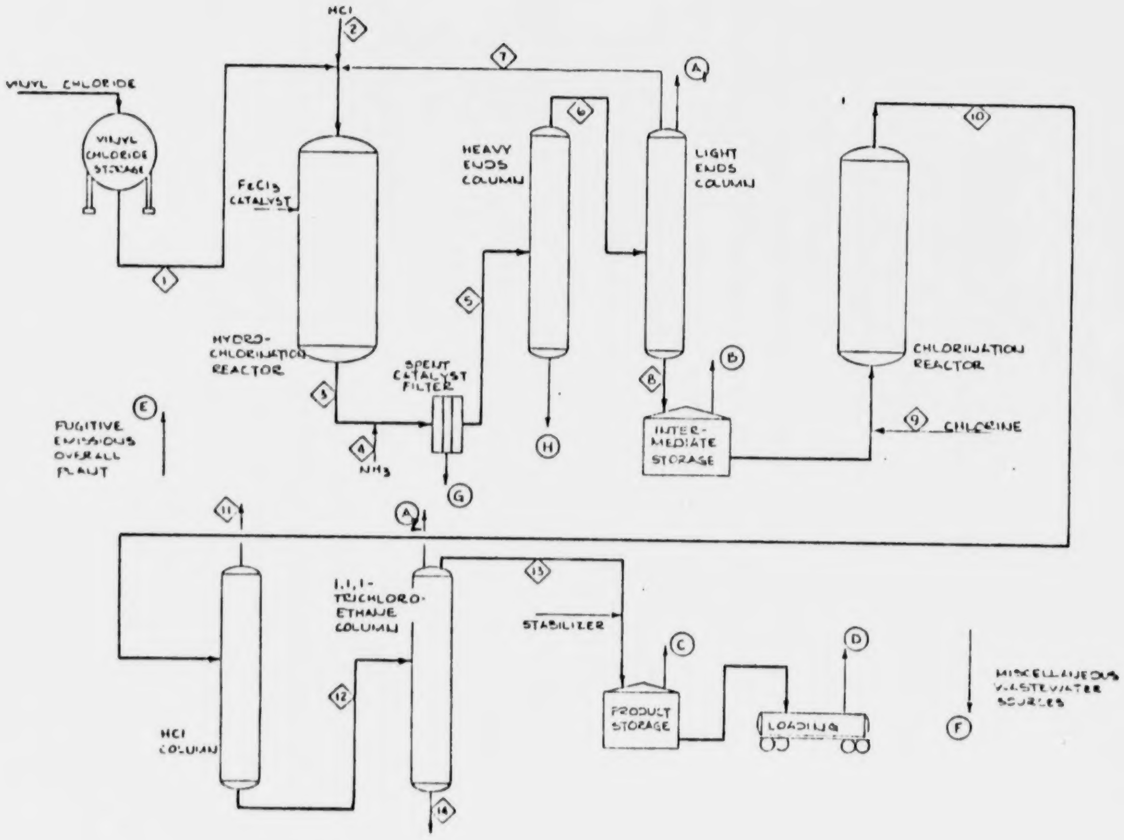

VINYL CHLORIDE
VINYL CHLORIDE STORAGE
1
HCl
2
FeCl3 CATALYST
HYDRO-CHLORINATION REACTOR
3
4
NH3
SPENT CATALYST FILTER
G
5
HEAVY ENDS COLUMN
H
6
7
LIGHT ENDS COLUMN
A
8
B
INTER-MEDIATE STORAGE
9
CHLORINE
CHLORINATION REACTOR
10
FUGITIVE EMISSIONS OVERALL PLANT
E
11
HCl COLUMN
12
A
1,1,1-TRICHLORO-ETHANE COLUMN
14
13
STABILIZER
PRODUCT STORAGE
C
LOADING
D
MISCELLANEOUS WASTEWATER SOURCES
F

Figure 2.2-1 Flow Diagram of the Production Process from Vinyl Chloride
(Hydroscience, 1979)

$$\text{Relative Quantity of Selected Compound} = \text{TRW/MRI Estimated kkg/kkg of Methyl Chloroform/DCE Produced} \div \text{TRW/MRI Total Estimated MC and DCE kkg/kkg of Methyl Chloroform Produced} \div \text{Compound Vapor Pressure at } 40^\circ\text{C}$$

$$\text{Relative Quantity of Methyl Chloroform (MC)} = 0.009 \text{ kkg/kkg} \div (0.009 \text{ kkg/kkg} + 0.0085 \text{ kkg/kkg}) \div 275^*$$

$$\text{Relative Quantity of DCE} = 0.0085 \text{ kkg/kkg} \div (0.0175 \text{ kkg/kkg}) \div 400^*$$

$\text{MC} = 1.869$ $\text{DCE} = 1.215$

$$\text{Percentage of MC} = \frac{1.869}{(1.869 + 1.215)} \times 100\% = 60.6\%$$

$$\text{Percentage of DCE} = \frac{1.215}{3.084} \times 100\% = 39.4\%$$

These calculations suggest that methyl chloroform would comprise over 60 percent of the product formulated in the hydrochlorination reactor. However, the second step of the vinyl chloride process chlorinates 1,1-dichloroethane at 400°C to produce methyl chloroform (EPA, 1979a; Hydroscience, 1979). Thus, even in the presence of a catalyst ($FeCl_3$), the 30-40°C hydrochlorination reaction could not produce any significant quantities of methyl chloroform. Also, the estimate given by TRW and MRI precludes the presence of vinyl chloride, an unlikely possibility (EPA, 1979a; TRW, 1975).

Hydroscience estimates that the composition of the light ends column consists of 0.1 weight percent of vinyl chloride, 2.5 weight percent of 1,1-dichloroethane and 97.4 weight percent of other non-organic gases (Hydroscience, 1979). Using these weight percents, vinyl chloride and 1,1-dichloroethane represent 4 percent ($0.1 \div 2.6$) and 96 percent ($2.5 \div 2.6$), respectively, of the volatile organic compounds present in the vent gases. These percentages are consistent with the known conversion rate of vinyl chloride to 1,1-dichloroethane (98 percent) identified previously (EPA, 1979a; Mannsville Chemical Products, 1978). The most likely reason for the higher percentage of vinyl chloride (4 percent rather than 2 percent) in the vent gases is its lower molecular weight, boiling point and density. Also, the volatility (vapor pressure) of vinyl chloride is significantly higher than that of 1,1-dichloroethane (see Table 2.2-1).

TABLE 2.2-1

SELECTED PHYSICAL PROPERTIES OF VINYL CHLORIDE, 1,1-DICHLOROETHANE AND METHYL CHLOROFORM

| | Vinyl Chloride | 1,1-Dichloroethane | Methyl Chloroform |
|---|---|---|---|
| Molecular Weight | 62.50 | 98.96 | 133.42 |
| Boiling Point (°C) | -13.4 | 57.3 | 74.1 |
| Density | 0.9106 | 1.1757 | 1.339 |
| Vapor Pressure (at 40°C, 1 Atm) | N/A | 400 mm | 275 mm |

Source: CRC, 1972

Note: Vapor Pressure of Methyl Chloroform Calculated by Linear Interpolation between 100 mm, 1 atm, 20.0°C and 400 mm, 1 atm, 54.6°C.

It should be noted that Hydroscience does not identify methyl chloroform as a product from the hydrochlorination reactor nor as a light ends column vent gas. Again, this is consistent with the first step of the vinyl chloride process.

Although methyl chloroform in the light ends column reported by MRI and TRW has been discounted and was not identified by Hydroscience, it may nevertheless be present in trace quantities (EPA, 1979a; TRW, 1975; Hydroscience, 1979). If methyl chloroform is present, the quantity could not exceed the 4 percent unreacted vinyl chloride identified by Hydroscience (Hydroscience, 1979). Assuming it is produced, the relatively (to vinyl chloride) high boiling point (74.1°C) and low vapor pressure (275 mm at 40°C, 1 atm) would minimize the quantity of gaseous methyl chloroform present in the light ends column. Since the vinyl chloride to 1,1-dichloroethane process temperature is 30-40°C, methyl chloroform and 1,1-dichloroethane would be liquids, whereas vinyl chloride would be a gas (boiling point: -13.4°C).

Therefore, we estimate that 1 percent of the 4 percent vinyl chloride identified by Hydroscience in the light ends column vent gases is methyl chloroform. Our confidence in this number is represented by a ±25% uncertainty. Dow Chemical Company has reported the use of a wet scrubber on the distillate column vent gases (Dow, 1978). Methyl chloroform is almost insoluble in water (1300 ppm) and therefore, the efficiency of the scrubber is limited to approximately 25 percent (±50%) (Appendix E; CRC, 1972). The primary removal agent is entrainment. Trapped methyl chloroform eventually evaporates during wastewater treatment. The quantity of methyl chloroform released by the light ends column or any step in the process can be calculated as follows:

$$\text{Methyl Chloroform Air Emissions} = \text{Annual Production of Methyl Chloroform by the Vinyl Chloride Process} \times \text{Volatile Organic Compound Uncontrolled Emission Factor} \times \text{Fraction of Methyl Chloroform in Volatile Organic Compounds} \times 1 - \text{Emission Control Efficiency}$$

(1) Assume MRI and TRW values - Total VOC = .0175 kkg/kkg (EPA, 1979a; TRW, 1975)

Methyl Chloroform = 179,000 kkg x .0175 kkg/kkg x (4% x 1%) x (1 - 25%)
= 0.940 kkg

(2) Assume Hydroscience value - Total VOC = .00019 kkg/kkg (Hydroscience, 1979)

Methyl Chloroform = 179,000 kkg x .00019 kkg/kkg x (4% x 1%) x (1 -25%)
= .0102 kkg

Since we have more confidence in the values estimated by Hydroscience (see previous discussion), the proposed emission is 0.2 kkg. The uncertainty of this value is +370% (MRI/TRW estimate and the upper bound of total production) and -95% (Hydroscience estimate and the lower bound of total production). The accuracy and error given this estimate have little significance because the upper bound or maximum emission represents only 0.0005 percent of the total quantity of methyl chloroform produced by the vinyl chloride process.

### 2.2.2.2 Emissions to the Air From Product Storage and Handling (Vents B, C, & D)

Uncontrolled emissions of volatile organic compounds (VOC's) to the air from product storage and the loading of tank cars and trucks and other transport containers in the vinyl chloride process are estimated in Table 2.2-2.

TABLE 2.2-2
UNCONTROLLED EMISSIONS DUE TO STORAGE AND HANDLING

| Source | Figure 2.2-1 -- Vent Designation | Ratio of Volatile Organic Compound (VOC) Emissions Per Quantity of Methyl Chloroform Produced |
|---|---|---|
| Storage Vents | | |
| o Intermediate Storage | B | 0.05 kkg/$10^3$ kkg* |
| o Product Storage | C | 1.19 kkg/$10^3$ kkg* |
| Handling - loading tank, trucks and cars, etc. | D | 0.61 kkg/$10^3$ kkg |

Source: Hydroscience, 1979; EPA, 1977c.

* See Appendix F

a) Air Emissions from Intermediate Storage (Vent B)

As discussed in Section 2.2.2.1 above, it is unlikely that measurable quantities of methyl chloroform could be found in the intermediate storage of 1,1-dichloroethane. However, the preceding analysis does suggest that small quantites of methyl chloroform may be present after the hydrochlorination of vinyl chloride. There is a mechanical refrigeration unit (MRU) on the storage tank vents (Dow, 1978).

A summary of the assumptions used to calculate air emissions from intermediate storage are presented below:

1) 1978 production = 179 x $10^3$ kkg (+6%, -7%) (EPA, 1979a and Section 2.2.1)

2) Uncontrolled emission rate for VOC from intermediate storage = 0.05 kkg/$10^3$ kkg (±25%)(Hydroscience, 1979)

The storage tank loss uncertainty is ±25% due to the following assumptions. The uncontrolled emission factor proposed by Hydroscience (Hydroscience, 1979) is based on a fixed roof tank which is half full. Diurnal temperature variations heat and thereby expel gases during daylight hours while cooling and drawing in air during darkness. These variations cause continuous vent losses during storage. The larger the air space above the liquid, the greater the daily losses are. Therefore, floating roof and non-vented storage tanks are sometimes employed.

Additional losses occur during filling and drawdown; these are also called working losses. These losses are the result of tank venting required to perform each procedure. Losses from this working phase are primarily dependent on throughput, loading method and the vapor pressure of the liquid.

Hydroscience assumed a temperature of 27°C for calculating the vapor pressure of methyl chloroform (Hydroscience, 1979). Submerged filling was assumed since it is commonly employed for volatile liquids.

The emission factor proposed by Hydroscience is a combination of the breathing losses (diurnal heating and cooling) and working losses (throughput). Assuming a normal throughput of 1 to 2 turnovers per week, breathing and working loss contributions to the emission factor are approximately equivalent.

If the tank is 75 or 25 percent full, the breathing losses vary by ±30%. Therefore, breathing losses are estimated to be accurate to ±30%, assuming the tank is half filled. Working losses are estimated to be accurate to ±20% due to fluctuations in the average temperature. A change of ±10°C will alter the losses by ±20 percent. Averaging the two losses and their errors translates into an overall ±25% error.

3) Fraction of methyl chloroform in the VOC - 0.04 percent (±25%) (Section 2.2.2.1)

4) Mechanical Refrigeration Unit (MRU) control efficiency = 85 percent (±5%)

The uncontrolled emission of methyl chloroform to the air from this source is:

$$\begin{aligned}\text{Air Emissions} &= 179 \times 10^3 \text{ kkg} \times 0.05 \text{ kkg}/10^3 \text{ kkg} \times (4\% \times 1\%) \times (1 - 85\%) \\ &= 0.000537 \text{ kkg}\end{aligned}$$

The uncertainty of this value is ±49%.

b) Air emissions from Product Storage (Vent C)

Emissions from product storage tank will be 100 percent methyl chloroform. The storage tanks are provided with an MRU on the vents (Dow, 1978).

A summary of the assumptions used to calculate air emissions from methyl chloroform product storage are presented below:

1) 1978 production = 179 x $10^3$ kkg (+6%, -7%) (EPA, 1979a and Section 2.2.1)

2) Uncontrolled emission rate for VOC from product storage = 1.19 kkg/$10^3$ kkg (±25%) (Hydroscience, 1979)

3) Fraction of methyl chloroform in the VOC = 100 percent

4) Mechanical Refrigeration Unit (MRU) control efficiency = 85 percent (±5%)

Therefore, the annual uncontrolled emission of methyl chloroform from product storage is:

$$179 \times 10^3 \text{ kkg} \times 1.19 \text{ kkg}/10^3 \text{ kkg} \times 100\% \text{ methyl chloroform} \times (1-85\%) = 32.0 \text{ kkg}$$

The uncertainty of this estimate is ±42% (see subsection (a) above).

c) Losses Due to Handling Techniques (Vent D)

Estimated air emissions are based on the submerged loading of methyl chloroform, at 27°C, into railroad tank cars and tank trucks (Hydroscience, 1979). Since the product being handled is raw methyl chloroform, we have assumed the VOC releases to be 100 percent product. A MRU is used during handling at the Dow Chemical Company facility (Dow, 1978).

A summary of the assumptions used to calculate air emissions from losses due to handling techniques are presented below:

1) 1978 production = 179 x $10^3$ kkg (+6%, -7%) (EPA, 1979a and Section 2.2.1)

2) Uncontrolled emission rate for VOC from losses and handling storage = 0.61 kkg/$10^3$ kkg (+30%, -10%) (Hydroscience, 1979)

3) Fraction of methyl chloroform in the VOC - 100 percent

4) Mechanical Refrigeration Unit (MRU) control efficiency = 80 percent (±5%)

Annual air emissions of methyl chloroform are:

179 x $10^3$ kkg x 0.61 kkg/$10^3$ kkg x 100% methyl chloroform x (1-85%)
= 16.4 kkg

This emission quantity is presented with an uncertainty of +45% -35%. The uncertainties for the total methyl chloroform production and the MRU are given above (see (a)). The uncontrolled air emission factor used by Hydroscience is predominatly dependent on the bulk liquid temperature. This temperature was assumed to be 27°C. A variation of +3°C or -5°C will account for a difference of +30% and -10%, respectively, in the emission factor. These errors were used to calculate the overall uncertainty for product handling.

The Freeport plant, Texas Division of Dow Chemical Company, estimated the annual evaporative losses of methyl chloroform due to product storage and handling at 41.4 tons or 37.6 kkg (Dow, 1978). The sum of the product storage and handling losses calculated above is 48.4 kkg. This represents a difference of only 22 percent between the Dow measurements and calculations and those presented in this report.

### 2.2.2.3 Emissions Due to the Distillation (Steam Stripping) of Methyl Chloroform (Vent $A_2$)

MRI and TRW estimated the loss of methyl chloroform from the distillation vent to be 0.0005 kkg/kkg of product (EPA, 1979a; TRW, 1975). Using the quantity produced by Dow in 1978, the annual air emission of methyl chloroform from this vent is:

$$179{,}000 \text{ kkg} \times 0.0005 \text{ kkg/kkg} \times 100\% \text{ methyl chloroform} \times (1-25\%)$$
$$= 67.1 \text{ kkg}$$

The uncontrolled emission factor estimated by Hydroscience is 0.19 kkg VOC/ $10^3$ kkg of methyl chloroform (Hydroscience, 1979). The VOC's are assumed to be 100 percent methyl chloroform. According to Dow, a 25 percent (±50%) efficient wet scrubber is used to control emissions from this source (Dow, 1978). The annual emission of methyl chloroform to the air is:

$$179 \times 10^3 \text{ kkg} \times 0.19 \text{ kkg}/10^3 \text{ kkg} \times 100\% \times (1 - 25\%) = 25.5 \text{ kkg}$$

The discrepancy between the 67.1 kkg (EPA, 1979a; TRW, 1975) and the 25.5 kkg (Hydroscience) values is probably due to the method of measuring the total air emissions from this part of the process. The EPA and TRW reports seem to include all air emissions from vent and wastewater stream. Therefore, the proposed emission of methyl chloroform from the distillation column vent is 25.5 kkg with an uncertainly of +160%, -15%. The +160% assumes the EPA and TRW value is correct and therefore is used as the upper bound. The -15% assumes minimum Dow market capture and maximum scrubber efficiency.

### 2.2.2.4 Fugitive Emissions (Vent E)

Sources of fugitive emissions within the production facilities include process pumps, compressors, process valves, and pressure-relief devices (Hydroscience, 1979).

A summary of the assumptions used to calculate air emissions from fugitive losses are presented below:

1) 1978 production = 179 x $10^3$ kkg (+6%, -7%) (EPA, 1979a and Section 2.2.1)

2) Uncontrolled emission rate for VOC from fugitive losses = 0.37 kkg/$10^3$ kkg (Hydroscience, 1979)

3) Fraction of methyl chloroform in the VOC = 100 percent

4) Emission Control Efficiency = 90 percent (±5%) (Hydroscience, 1979). Fugitive emissions are controlled through careful detection and correction of major leaks.

The emission of methyl chloroform to the air from fugitive emissions is:

$$179 \times 10^3 \text{ kkg} \times 0.37 \text{ kkg}/10^3 \text{ kkg} \times 100\% \times (1 - 0.9) = 6.62 \text{ kkg}$$

The uncertainty of this emission quantity is estimated at ±50% due to the following reasons: 1) it is estimated 100 percent of the VOC's is methyl chloroform; 2) the variability in leak detections and corrections; 3) maintenance procedures; and (4) Dow methyl chloroform production.

### 2.2.3 Emissions to Water (F)

Stream stripping of wastewater (Figure 2.2-1, emission F) is a source of VOC emissions.

A summary of the assumptions used to calculate emissions from wastewater treatment are presented below:

1) 1978 production = $179 \times 10^3$ kkg (+6%, -7%) (EPA, 1979a and Section 2.2.1)

2) Uncontrolled emission rate for VOC for wastewater treatment = 0.001 kkg/$10^3$ kkg (Hydroscience, 1979)

3) Fraction of methyl chloroform in the VOC = 100 percent

4) No emission control devices are included on the wastewater stream

The emissions to water are:

$179 \times 10^3$ kkg x .001 kkg/$10^3$ kkg x 100% x (1-0%) = 0.179 kkg

Another method for calculating the total water emissions is to use the EPA monitored level of methyl chloroform in the controlled aqueous effluent near the Dow plant. According to reported monitoring data, the levels of methyl chloroform ranged from 0.8 to 119 ppb by weight. We will assume the controlled aqueous effluent is 35 ppb methyl chloroform by weight, with an uncertainty of ±50% (EPA, 1977a). This is an EPA composite of available monitoring data (EPA, 1977a).

Based on typical daily water discharges from chemical plants similar in size to Dow's, we estimate that the water discharge of this plant is approximately 2 million gallons per day. The uncertainty of this figure is ±25%.

Using the above assumptions, the quantity of methyl chloroform in the controlled effluent discharge of the vinyl chloride based process can be calculated by multiplying the following factors:

A) 2,000,000 gpd of water discharges (±25%)

B) Operating days per year = 330 days/year
(±5% due to typical chemical plant down-time (Hydroscience, 1979))

C) Water density at 25°C = 1 kg/liter

D) 3.785 liters/gallon

E) Concentration of methyl chloroform in the effluent = $35 \times 10^{-9}$ kg methyl chloroform/kg of water (±50%)

Water emissions = $2 \times 10^{3}$ gallons/day x 330 days/year x 1 kg/liter x 3.785 liter/gallon x $35 \times 10^{-9}$ kg/kg = 87.4 kg or 0.0874 kkg

The estimates calculated using Hydroscience and EPA collected data represent a likely range for methyl chloroform residing after wastewater treatment. The range (0.0874 - 0.179 kkg), although quite large on a relative scale, represents an insignificant portion ($<$ 0.0001 percent) of the total methyl chloroform released to the environment.

For purposes of the materials balance, we estimate that the average of the two values, or 0.133 kkg, is the annual discharge. The uncertainty of this estimate is ±35% due to the uncertainty of the Hydroscience emission factor, total production of methyl chloroform by Dow daily water discharge quantities, annual days of operation, and inaccuracies in the EPA monitoring data and composite value.

### 2.2.4 Emissions to Air Due to Wastewater Treatment

During the wastewater treatment phase, volatile organic compounds (VOC's), such as methyl chloroform, trapped in aqueous effluent may be emitted to the air during aeration. We assume that 99 percent of the trapped methyl chloroform evaporates prior to being treated and the remaining 1 percent is treated. Thus, of every 100 parts of methyl chloroform in the aqueous effluent, 99 evaporate prior to water treatment, while the remaining part enters the treatment system. The error of the treated portion is +100%, -50% due to the insolubility in water (1300 ppm, Appendix E) and to the entrainment, not dissolution, of methyl chloroform in water.

Of the 1 percent treated, we assume that 5 percent is removed (evaporates, biodegrades, or is reformulated) during treatment and 95 percent is released intact in the controlled aqueous effluent. The assumption is based on the following:

- Methyl chloroform is not very soluble in water (1300 ppm - Appendix E)
- Biodegradation of methyl chloroform does not readily occur (Section 2.6)
- Chlorination of waste water does not remove (nor does it produce) any significant quantity of methyl chloroform. Also, indirect production of methyl chloroform does not readily occur. (Section 2.5)

The quantity removed from the controlled aqueous effluent is presented with an uncertainty of ±50%. The uncertainty represents an estimate based on the method of wastewater treatment and the likelihood of evaporation, biodegradation and reformulation during the treatment process. Therefore, the total quantity of methyl chloroform emitted to the air from process wastewater can be calculated as follows:

$$(0.133 \text{ kkg}) \times \frac{100\%}{95\%} \times \frac{99\%}{1\%} = 13.9 \text{ kkg}$$

where: 0.133 kkg = the quantity of methyl chloroform released to the water; (Section 2.2.3);

100%/95% = the ratio of the percentage of methyl chloroform that enters the treatment system and the unreacted percentage discharge into the control water effluent;

99%/1% = the ratio of the percentage of methyl chloroform released to the air prior to treatment and the percentage of this chemical that enters the treatment system.

The overall uncertainty of this figure is +107% and -62%. Although the proposed error is large, the estimated upper bound for wastewater treatment air emissions is only 0.02 percent of the methyl chloroform produced by Dow.

### 2.2.5 Emissions to Land (G and H)

Residue quantities (labeled G and H on Figure 2.2-1) disposed in landfills or incinerated are the only sources of methyl chloroform solid waste occurring at the plant (Hydroscience, 1979).

Solid waste is comprised of catalyst residues and organic wastes. They are estimated to contribute less than 0.1 percent to the total uncontrolled VOC emission rate at the model plant (Hydroscience, 1979). Hydroscience aggregates the loss due to landfill disposal and incineration into one number. For this analysis, we are assuming that half the Hydroscience emission rate will be considered to result from landfill disposal. The remaining half is incinerated and the ash is landfilled. A summary of the assumptions used to calculate this factor are presented below:

1) 1978 production = 179 x $10^3$ kkg (+6%, -7%) (EPA, 1979a; Section 2.2.1)

2) Uncontrolled emission rate for VOC's based on 50 percent of the residues being landfilled and 50 percent being incinerated = .0005 kkg/$10^3$ kkg (Hydroscience, 1979) (±100% - all or none of the solid wastes could be landfilled).

3) Fraction of methyl chloroform in the VOC = 0.04 percent (±25% - see Section 2.2.2.1 - emissions from points G and H in Figure 2.2-1 occur prior to the probable formulation of methyl chloroform).

4) No environmental controls are used during the landfill of sludge.

The calculation for this emission is:

Land emission = $179 \times 10^3$ kkg x .0005 kkg/$10^3$ kkg x 0.04% x (1-0%)
= $3.58 \times 10^{-5}$ kkg.

The uncertainty of this emission factor is estimated to be +103% -100%. This large uncertainty is mainly due to the 50/50 landfill to incineration estimate. Again, since the emission is so small ($< 2 \times 10^{-8}$ percent), large uncertainties have little significance.

### 2.2.6 Emissions to Air Due to the Incineration Disposal Method

The remaining 50 percent of the residues identified above are incinerated at the plant. Methyl chloroform, a volatile organic compound which is unstable at high temperatures, decomposes easily when incinerated. In addition, the process formulation temperature (approximately 400°C) is much lower than typical incineration temperatures (1000-1200°C). Therefore, we can assume a 95 percent destruction of the waste materials is achieved through incineration. The remaining 5 percent is released to the air. We also assume that there are no emission controls on the flue gases released by the incineration (Hydroscience, 1979). The high temperatures involved in the incineration process (1000-1200°C) precludes any quantifiable amount of methyl chloroform remaining in the ash residue. The fraction of methyl chloroform in the solid wastes from emission points G and H is 0.04 percent (see Section 2.2.2.1).

Assumptions used to calculate the emission factor are:

1) 1978 production = 179 x $10^3$ kkg (+6%, -7%) (EPA, 1979; Section 2.2.1)

2) Uncontrolled emission rate of residues (based on 50 percent of residues being incinerated) = 0.0005 kkg/$10^3$ kkg (±100% - all or none may be incinerated) (Hydroscience, 1979)

3) Fraction of methyl chloroform in VOC residues = 0.04 percent (±25% - see Section 2.2.2.1)

4) Incinerator efficiency = 95 percent destruction (±4% - see discussion above)

$$\text{Air emissions} = 179 \times 10^3 \text{ kkg} \times 0.0005 \text{ kkg}/10^3 \text{ kkg} \times 0.0004 \times (1 - 0.95)$$
$$= 1.79 \times 10^{-6} \text{ kkg}$$

The composite uncertainty of this emission figure is +131% and -100%. Incinerator air emissions of methyl chloroform represents approximately $10^{-9}$ percent of the total Dow methyl chloroform production.

### 2.2.7 Multimedia Environmental Losses

Figure 2.2-2 shows multimedia environmental losses of methyl chloroform from its production using the vinyl chloride process.

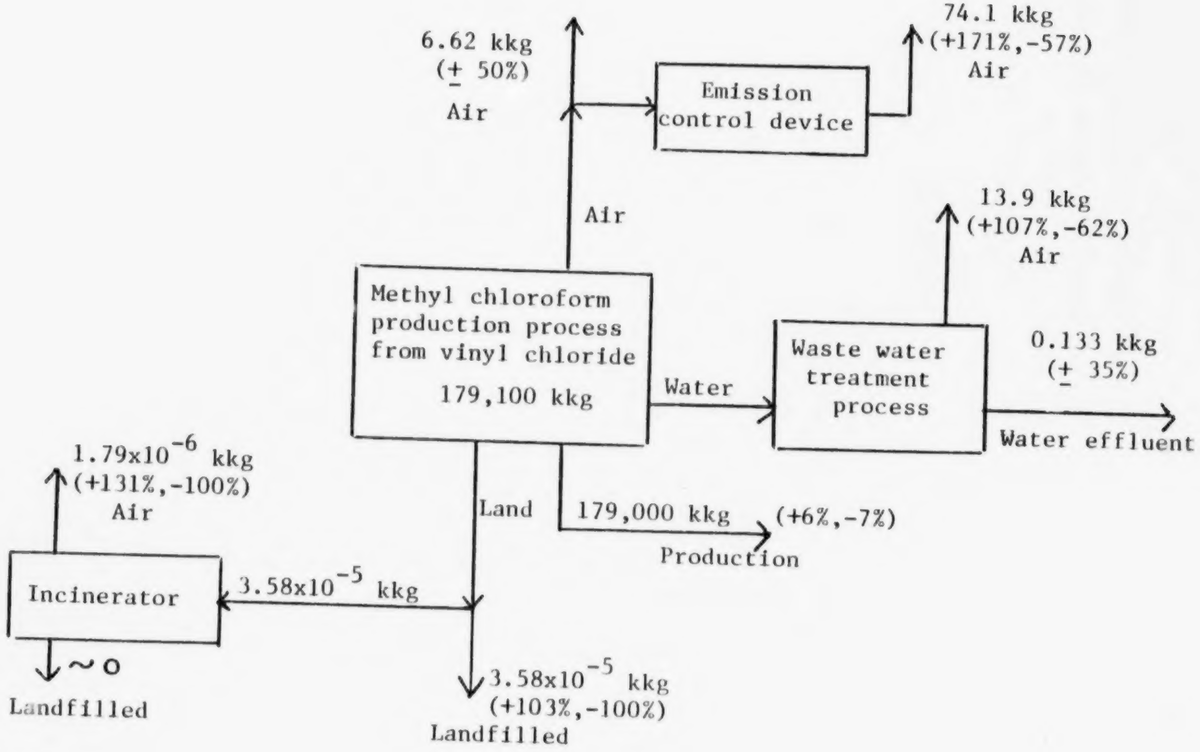

6.62 kkg
(± 50%)
Air
Emission control device
74.1 kkg
(+171%,-57%)
Air
Air
13.9 kkg
(+107%,-62%)
Air
Methyl chloroform production process from vinyl chloride
179,100 kkg
Water
Waste water treatment process
0.133 kkg
(± 35%)
Water effluent
1.79x10^-6 kkg
(+131%,-100%)
Air
Land
179,000 kkg
(+6%,-7%)
Production
Incinerator
3.58x10^-5 kkg
~0
Landfilled
3.58x10^-5 kkg
(+103%,-100%)
Landfilled

Figure 2.2-2 Multimedia Environmental Losses from the Vinyl Chloride-based Production Process

## 2.3 PRODUCTION OF METHYL CHLOROFORM FROM ETHANE

### 2.3.1 Production

Methyl chloroform is produced by the noncatalytic chlorination of ethane. This process is summarized by the following fractions (Hydroscience, 1979):

$$\underset{\text{(ethane)}}{CH_3\text{-}CH_3} \xrightarrow[-HCl]{+Cl_2} \underset{\text{(ethyl chloride)}}{CH_3\text{-}CH_2Cl} \xrightarrow[-HCl]{+\ Cl_2}$$

$$\underset{\text{(1,1-dichloroethane)}}{CH_3\text{-}CHCl_2} \xrightarrow[-HCl]{+Cl_2} \underset{\text{(1,1,1-trichloroethane)}}{CH_3CCl_3}$$

A flow diagram, representing this process for a model plant is shown in Figure 2.3-1 (Hydroscience, 1979). The model plant is based on an annual production capacity of 29,500 kkg (8760 hours of operation). According to Key and Standifer, this is the reported capacity of the Vulcan Materials Company plant at Geismar, Louisiana, the only company presently using the ethane process for the production of methyl chloroform (Hydroscience, 1979). The Hydroscience model plant flow diagram was used due to the lack of other available information on the Vulcan process.

The quantity of methyl chloroform produced in 1976 by the ethane process was 26,100 kkg or 9 percent of the total production (EPA, 1979a). Assuming that the percentage obtained for 1976 is also applicable for 1978, the quantity of methyl chloroform produced by the this method can be estimated by multiplying the 1978 total methyl chloroform production by 9 percent:

$$284{,}000 \text{ kkg} \times 0.09 = 25{,}500 \text{ kkg.}$$

This quantity was verified by verbal communication with Mr. Herb McGowan of Vulcan Materials Company (H. McGowan, 1979).

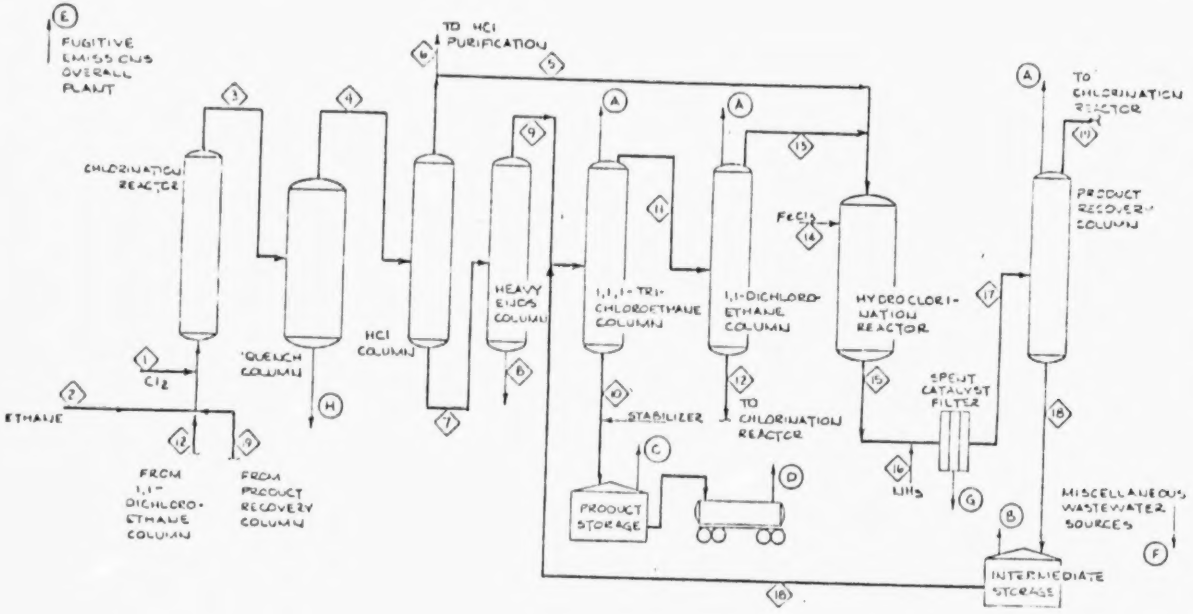

E
FUGITIVE EMISSIONS OVERALL PLANT
CHLORINATION REACTOR
1
$Cl_2$
2
ETHANE
12
FROM 1,1-DICHLORO-ETHANE COLUMN
19
FROM PRODUCT RECOVERY COLUMN
3
QUENCH COLUMN
H
4
HCl COLUMN
6
TO HCl PURIFICATION
5
7
HEAVY ENDS COLUMN
9
8
A
1,1,1-TRI-CHLOROETHANE COLUMN
10
STABILIZER
C
PRODUCT STORAGE
D
11
A
1,1-DICHLORO-ETHANE COLUMN
12
TO CHLORINATION REACTOR
13
$FeCl_3$
14
HYDROCLORI-NATION REACTOR
15
16
$NH_3$
SPENT CATALYST FILTER
G
17
A
TO CHLORINATION REACTOR
19
PRODUCT RECOVERY COLUMN
18
B
INTERMEDIATE STORAGE
18
MISCELLANEOUS WASTEWATER SOURCES
F

Figure 2.3-1 Flow Diagram of the Production Process from Ethane
(Hydroscience, 1979)

Also, since Vulcan began operation of a new 63,500 kkg production facility in 1979, we can assume the old facility was operating near capacity. This was typical of both the Dow and PPG expansion planning (EPA, 1979a). Downtime ranges from 5 to 15 percent annually depending on the age and maintenance of the plant and the chemical produced. Thus, the uncertainty of the above estimate is +2,000 kkg (95% x 29,500 kkg = 28,000 kkg) and -1,000 kkg (85% x 29,000 kkg = 25,000 kkg). The errors are +10%, -2%.

### 2.3.2 Emissions to Air

At the production site, uncontrolled emissions of volatile organic compounds (VOC's) to the atmosphere have been quantified from the following four sources:

1) plant process (distillation vents),

2) product storage and handling,

3) overall fugitive plant emissions, and

4) waste treatment (Hydroscience, 1979).

These emission rates are presented in Table 2.3-1 (Hydroscience, 1979). In order to calculate emissions at the site for these sources the following formula is used:

Methyl Chloroform
Air emissions (kkg) = 1978 production of methyl chloroform by
the ethane process ($10^3$kkg)
x volatile organic compound uncontrolled emission
factor (kkg/$10^3$kkg of production)
x fraction of methyl chloroform in VOC
x (1 - emission control efficiency*)

Quantities obtained using the above formula together with assumptions used in calculating these emissions from the four sources are discussed below.

---

*If applicable

Table 2.3-1 -- Estimates of Total Uncontrolled VOC Emissions from a Model Plant Producing Methyl Chloroform from Ethane[a]

| Source | Vent Designation (Fig.III-2) | VOC Emissions Ratio (g/kg)[b] | VOC Emissions Rate (kg/hr) |
|---|---|---|---|
| Distillation vents | A | 0.21 | 0.7 |
| Storage vents | | | |
| Recycle storage | B | 0.06[c] | 0.19[c] |
| Product storage | C | 0.98[c] | 3.3[c] |
| Handling | D | 0.61 | 2.1 |
| Fugitive | E | 1.69 | 5.7 |
| Secondary | | | |
| Wastewater treatment | F | 0.001 | 0.004 |
| Incineration of residues and/or landfill | G,H | 0.001 | 0.01 |
| Total | | 3.4 | 11.6 |

[a] Uncontrolled emissions are emissions from a process for which there are no control devices other than those necessary for economical operation.

[b] g of emission per kg of methyl chloroform produced.

[c] see Appendix F

Source: Hydroscience, 1979

### 2.3.2.1 Plant Process

The only significant process emission occurs when gas is vented at the distillation-column reflux condenser vents (labled A in Figure 2.3-1) (Hydroscience, 1979). The combustion of vent gas is employed to control emissions at the model plant (Hydroscience, 1979). Assumptions used to estimate methyl chloroform loss from these vents are:

1) 1978 production = 25.5 x $10^3$kkg (+10%, -2%) (EPA, 1979a; McGowan, 1979; Section 2.3.1)

2) uncontrolled emission rate = 0.21 kkg/$10^3$kkg (Hydroscience, 1979)

3) fraction of methyl chloroform in VOC (see Table 2.3-2) = 0.67 (±25%) (Hydroscience, 1979)

4) efficiency of incineration as control device = 95 percent (±4%) (Hydroscience, 1979 and Section 2.2.6)

Using the above information in the formula described in the previous section, air emissions are calculated as follows:

$$\text{Air Emissions} = 25.5 \times 10^3 \text{ kkg} \times 0.21 \text{ kkg}/10^3 \text{ kkg} \times 0.67 \times (1 - .95) = 0.179 \text{ kkg}$$

Table 2.3-2 -- Estimated Composition of Distillation Vent Gas from Model Plant Producing Methyl Chloroform from Ethane

| Component | Composition (wt %) | Weight Percent Volatile Organic Compounds |
|---|---|---|
| Methyl chloroform | 35 | 67 |
| Ethylene dichloride | 17 | 33 |
| Nitrogen, oxygen | 48 | - |
| Total | 100 | 100 |

Source: Hydroscience, 1979

The composite uncertainty of the emission factor is estimated to be ±84%. The primary reason for this uncertainty is the variance in the effeciency attributed to the vent gas incinerator. For example, a two percent decrease in the emission control efficiency increases the air emission by 40 percent.

Air emissions (93% efficient incinerator) = 25.5 x $10^3$ kkg x 0.21 kkg/$10^3$ kkg x 0.67 x (1-.93) = .251 kkg

Increased Air Emission = .251 kkg/.179 kkg = 1.40

### 2.3.2.2 Product Storage and Handling

VOC emissions result from the intermediate storage (labeled B in Figure 2.3-1 ), product storage (labeled C in Figure 2.3-1) and the loading of tank cars and trucks (label D in Figure 2.3-1). Handling and storage emissions are controlled by a refrigerated vapor recovery system (Hydroscience, 1979; D. Phillips, 1979). Assumptions used to calculate methyl chloroform air emissions from product storage and handling are:

1) 1978 production = 25.5 x $10^3$ kkg (+10%, -2%) (EPA, 1979a; McGowan, 1979; Section 2.3.1)

2) Uncontrolled VOC emission rates from Table 2.3-1 (Hydroscience, 1979; Appendix F; Section 2.2.2.2):

    A) Intermediate storage = 0.06 kkg/$10^3$ kkg (±20%)

    B) Product storage = 0.98 kkg/$10^3$ kkg (±20%)

    C) Handling = 0.61 kkg/$10^3$ kkg (+30%, -10%)

3) Based on the suggested turnover volume identified in Table 2.3-3 (Hydroscience, 1979),

    A) Intermediate Storage = 20% (±25%)

    B) Product storage = 100%

    C) Handling = 100%

4) Efficiency of vapor recovery system = 85 percent (±5% (Hydroscience, 1979 and Section 2.2.2.2)

Therefore, the calculations for storage and handling emissions are:

A) Intermediate storage

Air emissions (kkg) $= 25.5 \times 10^3$ kkg $\times$ 0.06 kkg/$10^3$ kkg $\times$ 0.20 $\times (1 - .85)$

= 0.0459 kkg (+47%, -39%)

B) Product storage

Air emissions $= 25.5 \times 10^3$ kkg $\times$ 0.98 kkg/$10^3$ kkg $\times$ 1.00 $\times (1 - .85)$ = 3.75 kkg (+40%, -39%)

C) Handling

Air emissions $= 25.5 \times 10^3$ kkg $\times$ 0.61 kkg/$10^3$ kg $\times$ 1.00 $\times (1 - .85)$

= 2.33 kkg (+46%, -35%)

Total handling and storage emissions = 0.04 kkg + 3.75 kkg + 2.33 kkg

= 6.13 kkg

The uncertainty of the sum of the emission factors is estimated to be +61%, -52%.

Uncertainties for storage and handling emission rates are the same as those identified in Section 2.2.2.2. Emission rates for intermediate and product storage represent only "working" losses because the storage tanks identified by Hydroscience are not normally vented (Hydroscience, 1979). This is typical of smaller tanks. Thus, breathing losses should not be present at Vulcans methyl chloroform storage facility. Since loading and unloading does requre venting, estimated working losses are presented and an uncertainty of ±20 percent has been given to these values (See Section 2.2.2.2 and Appendix F).

The fraction of methyl chloroform in intermediate storage releases is a function of the number of tank turnovers and the quantity per turnover. Calculations suggest that the quantity of methyl chloroform transferred represents 20 percent of the total for intermediate storage.

Product storage and handling air emissions are assumed to contain 100 percent methyl chloroform.

Table 2.3-3 -- Storage Tank Data for Methyl Chloroform (Ethane Feed) Model Plant

| | Tank | | |
|---|---|---|---|
| | Intermediate | Intermediate | Product |
| Contents | 1,1 Dichloro-ethane | Crude, Methyl chloroform | Refined, Methyl chloroform |
| Number of tanks | 4 | 2 | 4 |
| Tank size (m)$^3$ | 55 | 29 | 174 |
| Turnovers per year | 11 | 44 | 73 |
| Bulk temperature (°C) | 27 | 27 | 27 |

Source: Hydroscience, 1979

### 2.3.2.3 Overall Fugitive Plant Emissions

Fugitive VOC emissions (labeled E in Figure 2.3-1) have been estimated (Hydroscience, 1979) based on the average number of process pumps, compressors, process values, and pressure relief valves handling VOC at the model plant. Assumptions used in the calculation include:

A) 1978 production = 25.5 x $10^3$ kkg (+10, -2%) (EPA, 1979a; McGowan, 1979; Section 2.3.1)

B) Uncontrolled VOC emission rate = 1.69 kkg/$10^3$ kg (±20%) (Hydroscience, 1979; Table 2.3-1)

C) Fraction of methyl chloroform in VOC (fugitive emission composition is estimated to be comparable to the composition of the vent gases, see Table 2.3-1) = 67 percent (±25%) (Section 2.3.2.1)

D) Efficiency of control device (detection and correction of major leaks) = 90% (±5%) (Hydroscience, 1979).

The calculation of methyl chloroform air emissions are:

$$\text{Air emissions} = 25.5 \times 10^3 \text{ kkg} \times 1.69 \text{ kkg}/10^3 \text{ kg} \times 0.67 \times (1 - .90)$$
$$= 2.89 \text{ kkg}$$

The uncertainty of the emission factor is estimated to be +60% -59% . The uncertainty is due to the variability in leak detection capability and maintenance procedures. A plant inspection would be required to ascertain the adherence to leak detection and correction procedures. The overall fugitive emission uncertainty (especially the upper bound) seems consistent with good economic operation.

### 2.3.3 Emissions to Water

Steam stripping of wastewater (labeled F in Figure 2.3-1) is a source of VOC emissions. Assumptions used in calculating methyl chloroform water emissions are:

1) 1978 production = $25.5 \times 10^3$ kkg (+10%, -2%) (EPA, 1979a; McGowan, 1979; Section 2.3.1)

2) Uncontrolled emission rate for wastewater treatment = 0.001 kkg/$10^3$ kg (Hydroscience, 1979)

3) Fraction of methyl chloroform in VOC (maximum value assumed) = 100%

4) No control device used due to low concentrations.

The emissions to water are:

$$\text{Water emissions} = 25.5 \times 10^3 \text{ kkg} \times .001 \text{ kkg}/10^3 \text{ kkg} \times 1.00$$
$$= .0255 \text{ kkg}$$

Another method for calculating the total water emissions uses the EPA monitored level of methyl chloroform in the controlled aqueous effluent near the Vulcan plant. According to reported monitoring data, the levels of methyl chloroform ranged from 2 - 16,500 ppb by weight (EPA, 1977a). We will assume the average controlled aqueous effluent (composite of EPA monitoring data) is 169 ppb methyl chloroform by weight; with an uncertainty of ±50% (EPA, 1977a).

Based on typical daily water discharges from chemical plants similar in size to Vulcan's, we estimate that the water discharge of this plant is approximately 300,000 gallons per day. The uncertainty of this figure is ±25%.

Using the above assumptions, the quantity of methyl chloroform in the controlled effluent discharge of the ethane based production process can be calculated by multiplying the following factors:

A) 300,000 gallons of water discharged per day (±25%)

B) Operating days per year =

$$\frac{25{,}500 \text{ kkg}}{29{,}500 \text{ kkg}} \times 365 \text{ days} = 316 \text{ days } (+10\%, -2\ \%) \text{ (See Section 2.3.1)}$$

C) Water density at 25°C = 1 kg/liter

D) 3.785 liters/gallon

E) Concentration of methyl chloroform in the effluent = $169 \times 10^{-9}$ kg methyl chloroform/kg of water

Total methyl chloroform in controlled effluent discharge =
300,000 gallons/day x 316 days/year x 1 kg/liter x
3.785 liter/gallon x 169 x $10^{-9}$ kg/kg = 60.6 kg or 0.0606 kkg

The Hydroscience and the EPA effluent monitoring data estimates represent the likely range of methyl chloroform remaining after wastewater treatment. The range, although quite large on a relative scale, represents an extremely minor portion ( $<$ .0002 percent) of the total methyl chloroform produced at the Vulcan facility.

For the purposes of the materials balance, we estimate that the average of the two calculated emissions, or 0.0430 kkg, is the annual discharge. The uncertainty of this estimate is ±41 percent based on the uncertainty of the Hydroscience emission factor, daily water discharge quantities and inaccuracies in the EPA monitoring data.

### 2.3.4 Emissions to the Air Due to Wastewater Treatment

During the wastewater treatment phase, volatile organic compounds (VOC's), such as methyl chloroform, trapped in the aqueous effluent may be emitted to the air due to the aeration process in the treatment system. We assume that 99 percent of the trapped methyl chloroform evaporates prior to being treated and the remaining 1 percent is treated by the system. Thus, of every 100 parts of methyl chloroform in the aqueous effluent, 99 evaporate prior to water treatment, while the remaining part enters the treatment system. The estimated uncertainty is +100% -50% (see Section 2.2.4). Of the 1 percent treated, we assume that 5 percent of the methyl chloroform is removed during treatment of activated sludge and 95 percent is released intact in the controlled aqueous effluent (see Section 2.2.4). The 95 percent represents the calculated emission of methyl chloroform to water in the preceding section. Therefore, the total quantity of methyl chloroform emitted to the air from process water can be calculated as follows:

$$(0.0430 \text{ kkg}) \left(\frac{100\%}{95\%}\right) \left(\frac{99\%}{1\%}\right) = 4.48 \text{ kkg}$$

Where:

0.0430 kkg = the amount of methyl chloroform released to the water by the wastewater treatment system.

100%/95% = the ratio of the percentage of methyl chloroform that enters the treatment system and the untreated percentage discharged into the controlled water effluent.

99%/1% = the ratio of the percentage of methyl chloroform released to the air prior to treatment and the percentage of this chemical that enters the treatment system.

The overall uncertainty of this figure is +109% and -66% due to the uncertainty of the evaporation rate and the removal efficiency of the treatment system.

### 2.3.5 Emissions to Land

Residue quantities (labeled G and H in Figure 2.3-1) disposed in landfills are the only source of VOC solid waste estimated to occur at the model plant (Hydroscience, 1979). Assumptions used to calculate the emission factor are:

1) 1978 production = 25.5 x $10^3$ kkg (+10%, -2%) (EPA, 1979a; McGowan, 1979; Section 2.3.1)

2) Uncontrolled emission rate (based on 50 percent of the residues being landfilled and 50 percent being incinerated = .0005 kkg/$10^3$ kkg (±100%) (Hydroscience, 1979; Section 2.2.5)

3) Fraction of methyl chloroform in VOC = 30 percent (±50%). The fraction was estimated by assuming

- the weight of the residues from emissions labeled G and H were equal.
- 50 percent of the spent catalyst is methyl chloroform.
- 10 percent of the solid wastes from the quench column is methyl chloroform.

A ±50% uncertainty has been assigned to this value. It is unlikely that the fraction of methyl chloroform is greater than 45 percent, nor less than 15 percent of the total VOC residues.

4) No control device used due to low concentrations.

The calculation for this emission is:

Quantity of methyl
chloroform landfilled $= 25.5\ 10^3 \text{kkg} \times .0005\ \text{kkg}/10^3\ \text{kkg} \times 0.30$
$= 0.00383$ kkg

The uncertainty of the land emission is estimated to be +112%,-100%. It is primarily due to the assumption that 50 percent of the residues are landfilled.

### 2.3.6 Emissions to the Air Due to the Incineration Disposal Method

The remaining 50 percent of the residue is incinerated at the plant. We assume a 95 percent destruction of the waste materials is achieved through incineration, with the remaining 5 percent being released to the air. We also assume that there are no emission controls on the flue gases released by the incinerator. The high temperature involved in the incineration process precludes any quantifiable amount of methyl chloroform remaining in the ash residue.

Assumptions used to calculate the emission factor are:

1) 1978 production = $25.5 \times 10^3$ kkg (+10, -2%) (EPA, 1979a; McGowan, 1979; Section 2.3.1)

2) Uncontrolled emission rate of residues (based on 50 percent of residues being incinerated) = .0005 kkg/$10^3$ kkg (±100%) (Hydroscience, 1979; Section 2.2.5)

3) Fraction of methyl chloroform in VOC residues = 30 percent (±50%) (Section 2.3.5 above)

4) Incinerator efficiency = 95 percent destruction (±4%) (see Section 2.2.6)

Air emissions = $25.5 \times 10^3$ kkg x 0.0005 kkg/$10^3$ kkg x 0.30 x (1 - 0.95)
= 0.000191 kkg

The uncertainty of this emission figure is +138 percent and -100 percent due to the percentage of the emission factor estimate portioned to incineration, the assumption of no control on the emission from the incinerator, and the efficiency of the incinerator.

### 2.3.7 Multimedia Environmental Losses

Figure 2.3-2 shows multimedia environmental losses of methyl chloroform from its production using the ethane process.

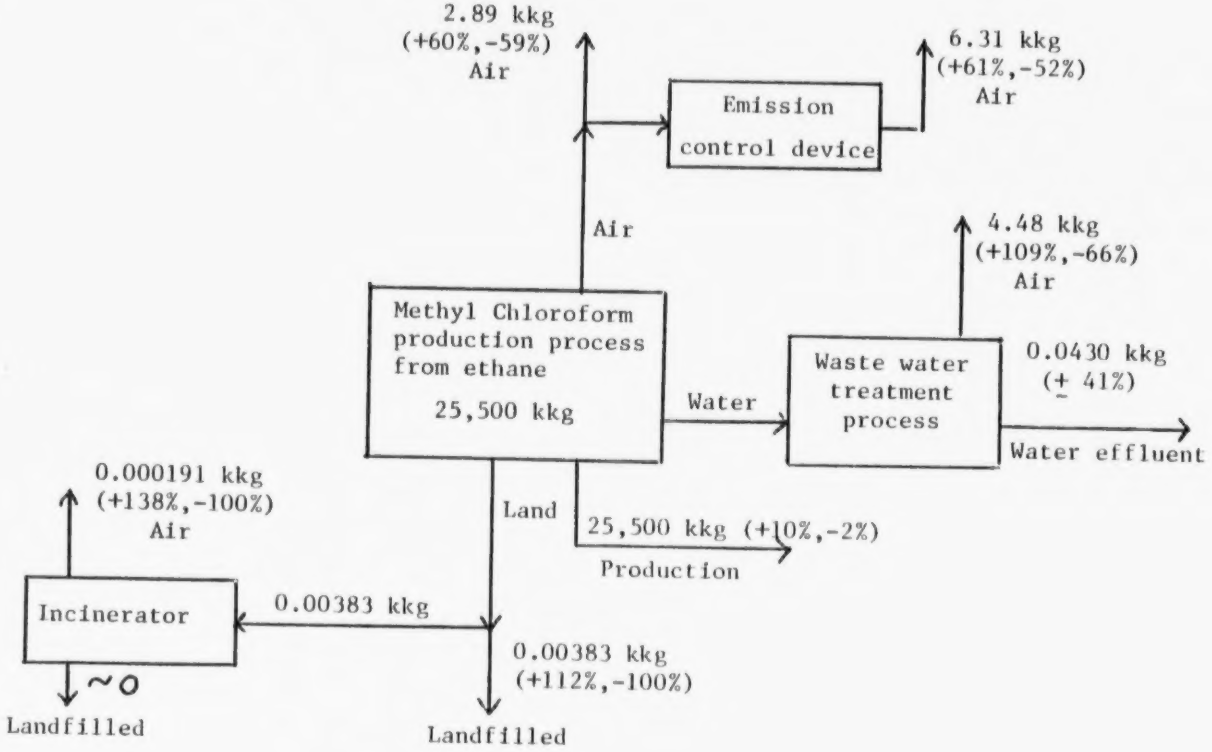

2.89 kkg
(+60%,-59%)
Air
Emission
control device
6.31 kkg
(+61%,-52%)
Air
Air
4.48 kkg
(+109%,-66%)
Air
Methyl Chloroform
production process
from ethane
25,500 kkg
Water
Waste water
treatment
process
0.0430 kkg
(± 41%)
Water effluent
0.000191 kkg
(+138%,-100%)
Air
Land
25,500 kkg (+10%,-2%)
Production
Incinerator
0.00383 kkg
0.00383 kkg
(+112%,-100%)
~0
Landfilled
Landfilled

Figure 2.3-2 Multimedia Environmental Losses from the Ethane-based Production Process

## 2.4 VINYLIDENE CHLORIDE PROCESS

### 2.4.1 Production

Methyl chloroform can be produced by the vinylidene chloride method. The main reaction involved in this process is the hydrochlorination of vinylidene chloride in the presence of a $FeCl_3$ catalyst. It is represented as follows:

$$CH_2 = CCl_2 + HCl \xrightarrow{FeCl_3} CH_3CCl_3.$$

An average yield rate of 98 percent or more is achieved with this method (EPA, 1979a; Mannsville Chemical Products, 1978). Unconverted materials are usually recycled or wasted. A more detailed discussion of this production process is presented in Appendix A.

Until late 1978, Pittsburgh Plate Glass (PPG) produced methyl chloroform by the vinylidene chloride method (SRI, 1975; EPA, 1979a; PPG, 1979; CPS, 1978). By January 1979, the new production method was operating at full capacity. The vinylidene chloride plant presently fills any requirements in excess of those supplied by the new process. Therefore, in 1979, the production of methyl chloroform by the vinylidene chloride method will be approximately 25,000 kkg. Information on this newly developed production process was unavailable at the time this report was prepared. Informed sources have suggested that the new process probably uses vinyl chloride as a raw material.

Since this report presents a material balance of methyl chloroform for the year 1978, it is appropriate to calculate the quantity of methyl chloroform produced from vinylidene chloride in 1978.

According to Midwest Research Institute (MRI), the quantity of methyl chloroform produced in 1976 by the vinylidene chloride method

(EPA, 1979a) was estimated at 79,500 kkg or 28 percent of the total production. Assuming that the percentage obtained for 1976 is also applicable for 1978, the quantity of methyl chloroform produced by this process can be estimated as follows:

| Production from Vinylidene Chloride Method | = | 1978 Total U.S. Production of Methyl Chloroform | x | Percent Market Capture of Process |
|---|---|---|---|---|
| 79,500 kkg | = | (284,000 kkg) | x | (0.28) |

This figure has an uncertainty of +0% and -14%. The +0% error is due to the known maximum operating capacity of the PPG Lake Charles plant (EPA, 1979a). In 1976, the maximum plant capacity was achieved thus verifying this figure as an actual upper limit (EPA, 1979a). The lower limit (-14%) assumes PPG has expanded plant capacity to meet their future expected percent of the market; that is, 24 percent (EPA, 1979a; Mannsville Chemical Products, 1978; CEH, 1979). This percentage is also consistent with the lower limit for operating days per year; or 310 days (Hydroscience, 1979; Section 2.2.3).

### 2.4.2 Emissions to Air

According to MRI, methyl chloroform is not emitted to the air from the vinylidene chloride process (EPA, 1979a). We speculate that some emissions to the air from this process must exist.

With little available information on the vinylidene chloride method and by using information obtained on the vinyl chloride-based production process (a similar process) (Hydroscience, 1979), we arrived at a derived flow diagram which probably represents the actual production process of methyl chloroform from vinylidene chloride. This derived flow diagram is presented in Figure 2.4-1. According to the derived flow diagram, methyl chloroform emissions to the air can occur from the following possible sources: 1) the hydrochlorinator vent; 2) the methyl chloroform column vent; 3) storage and handling techniques; and 4) fugitive emissions.

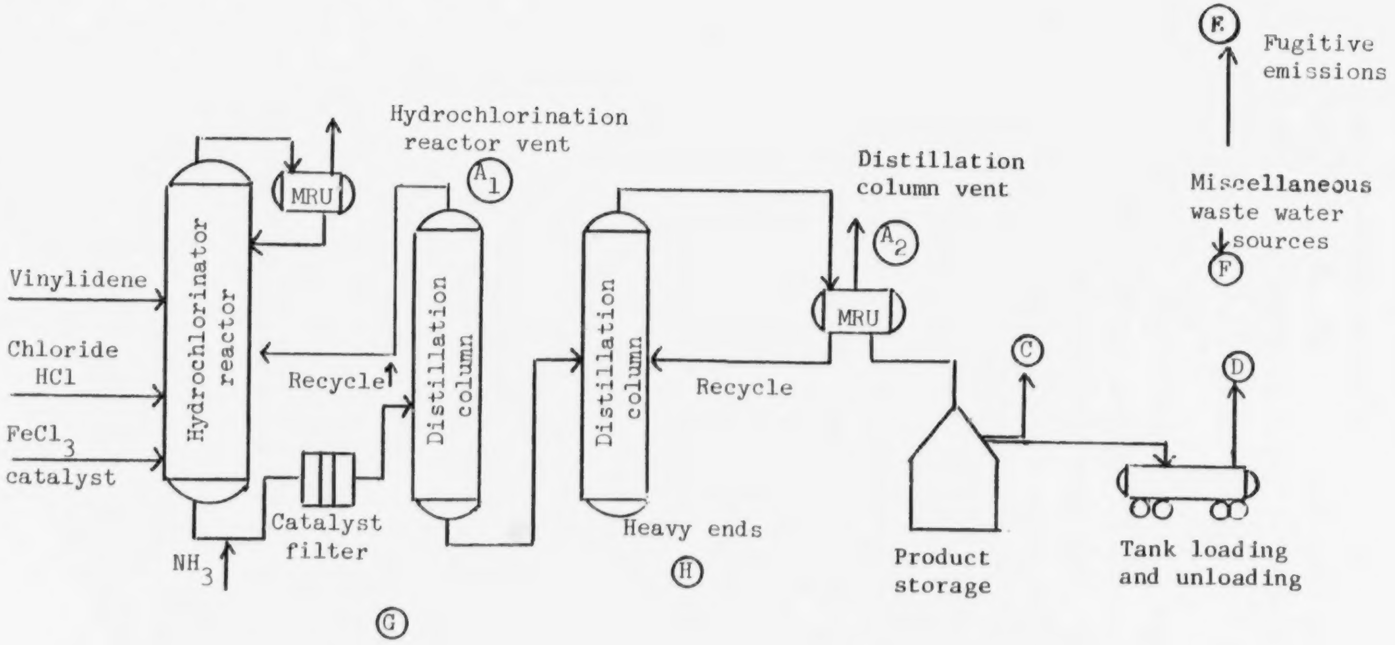

E
Fugitive emissions
Hydrochlorination reactor vent
$A_1$
MRU
Distillation column vent
$A_2$
Miscellaneous waste water sources
F
Vinylidene
Chloride
HCl
$FeCl_3$ catalyst
Hydrochlorinator reactor
Recycle
Distillation column
Distillation column
MRU
C
D
Recycle
Catalyst filter
$NH_3$
Heavy ends
H
Product storage
Tank loading and unloading
G

Figure Derived Flow Diagram of the Production Process from Vinylidene Chloride

Since there is no information on the emissions of methyl chloroform to the air from the vinylidene chloride based production process, we assume that the use of emission factors obtained for similar emission sources in the ethane and vinyl chloride-based production processes are applicable for the calculation of the emission quantities of methyl chloroform from the vinylidene chloride method.

Emissions are calculated with and without environmental control devices. Both calculations are presented in this report to account for the lack of available environmental control information. For each source of emission, the most probable type of control technology is indicated. Also, an evaluation of the likelihood that PPG uses the indicated control technology is performed.

Total multimedia environmental losses (Figure 2.4.2) are calculated by assuming that PPG uses appropriate emission control technologies.

In order to calculate emissions at the production site, the following formulae are used.

$$\begin{array}{c} \text{Uncontrolled} \\ \text{Methyl Chloroform} \\ \text{Emissions} \end{array} = \begin{array}{c} \text{1978 Productions of Methyl} \\ \text{Chloroform by the Vinylidene} \\ \text{Chloride Process} \end{array} \times \begin{array}{c} \text{Volatile Organic} \\ \text{Compound Uncontrolled} \\ \text{Emission Factor} \end{array} \times \begin{array}{c} \text{Fraction of Methyl} \\ \text{Chloroform in VOC} \end{array}$$

$$\begin{array}{c} \text{Controlled} \\ \text{Methyl Chloroform} \\ \text{Emissions} \end{array} = \begin{array}{c} \text{Uncontrolled} \\ \text{Methyl Chloroform} \\ \text{Emissions} \end{array} \times \begin{array}{c} \text{1-Emission} \\ \text{Control} \\ \text{Efficiency} \end{array}$$

#### 2.4.2.1 Emission to Air From the Hydrochlorinator Vent (Vent $A_1$)

Process emissions occur when gases are released from the hydrochlorination reactor vent ($A_1$). Although it is unlikely, PPG may not use an emission control device on the hydrochlorination reactor.

Therefore, it is assumed that these vent gases are controlled with a mechanical refrigeration unit (MRU). The controlled emission is included in the total multimedia environmental losses.

Assumptions used to estimate the loss of methyl chloroform from the hydrochlorination reactor vent are:

1) 1978 Production = 79,500 kkg (+0%, -14%) (EPA, 1979a; Hydroscience, 1979; and Section 2.4.1)

2) Uncontrolled VOC emission factor = 2 kkg/$10^3$ kkg (+350%, -90%)

The emission factor was estimated using vinyl chloride and ethane process emission rates for both hydrochlorination reactor vents (.00019 kkg/kkg and .00021 kkg/kkg) (Hydroscience, 1979) and the TRW/MRI estimate for the vinyl chloride process (0.009 kkg/kkg) (TRW, 1975; EPA, 1979a). The proposed estimate reflects a greater confidence in the Hydroscience report (Hydroscience, 1979). The upper and lower bounds of the emission factor are the TRW/MRI and Hydroscience estimates.

3) fraction of methyl chloroform in VOC = 98 percent (+1%, -8%)

The yield rate of methyl chloroform from vinylidene chloride is 98 percent (EPA, 1979a; Mannsville Chemical Products, 1978). An upper bound of 99 percent is possible (although not likely) and an economic lower bound is approximately 90 percent.

4) Vapor recovery system (MRU) effeciency = 85 percent (±5%) (Hydroscience, 1979; Section 2.2.2.2)

Using the above information in the formulae described in the previous section, uncontrolled and controlled air emissions are calculated as follows:

Uncontrolled Air Emissions = 79,500 kkg x .002 kkg/kkg x 0.98 = 156 kkg

Controlled Air Emissions = 156 kkg x (1 - 0.85) = 23.4 kkg

The uncertainty assigned to the controlled air emission is +352% and -97%. The large uncertainty is due primarily to the large variance in the emission factor. It should be noted that the upper bound of this contolled emission represents less than 0.2 percent of the methyl chloroform produced by the vinylidene chloride process. Even if the hydrochlorination reactor vent is not equipped with an emission control, the estimated upper limit contributes less than 0.9 percent of the methyl chloroform produced by this process. In either case, the quantities released are not significant.

### 2.4.2.2 Emissions to the Air from the Distillation Column

It is estimated that 0.0005 kkg per kkg of methyl chloroform produced is released to the air from the methyl chloroform distillation column in the vinyl chloride-based production process (EPA, 1979a). If this emission factor is also applicable for the vinylidene chloride-based production process, then the following can be used to calculate the uncontrolled and controlled emissions:

1) 1978 production 79,500 kkg (+0%, -14%) (Section 2.4.1)

2) Uncontrolled VOC emission factor = 0.0003 kkg/kkg product (+67%, 33%) (See 2.4.2.1 - uncontrolled VOC emission factor). The upper bound is the TRW/MRI estimate (0.0005 kkg/kkg) and the lower bound is the Hydroscience estimate (0.0002 kkg/kkg) (EPA, 1979a; TRW, 1975; Hydroscience, 1979).

3) Fraction of methyl chloroform in VOC = 100%

4) Vapor Recovery System (MRU) efficiency = 85% (±5%) (Hydroscience, 1979; Section 2.2.2.2)

The uncontrolled and controlled emissions to the air are calculated as follows:

Uncontrolled Air Emission = 79,500 kkg x 0.0003 kkg/kkg x 1.00 = 23.9 kkg

Controlled Air Emission = 23.9 kkg x (1 - 0.85) = 3.59 kkg

As shown on Figure 2.4-1, it is assumed that the distillation column has a mechanical refrigeration unit. This type of emission control is typical of volatile organic compound processes. Therefore, the controlled air emission is included in the multimedia environmental losses. The uncertainty of the estimated emissions is +75%, -49%. Again, the uncertainty given to the distillation column emission is large. But, as noted earlier, although the range of estimated emissions is large, the relative quantity of methyl chloroform released to the quantity produced is not significant ( $<$ .01 percent).

### 2.4.2.3 Emissions to the Air from Product Storage and Handling Techniques

Uncontrolled emission of methyl chloroform to the air from product storage and loading of tank cars and trucks in the vinyl chloride-based production process is estimated at 1.19 g/kg and 0.61 g/kg of methyl chloroform produced respectively (Hydroscience, 1979; Appendix F). The facility operated by PPG is probably similar to that of Dow. Thus, tank sizes should be similar to those of Dow, although not as many are required. Assuming similar tank sizes, the above emission factors are also applicable for the vinylidene chloride method. Emissions of methyl chloroform from the above sources can be calculated using the following assumptions:

1) 1978 production = 79,500 kkg (+0%, -14%)(see Section 2.4.1)

2) Uncontrolled VOC emission factors (See Section 2.2.2.2)

   a) product storage = 0.00119 kkg/kkg (±25%)

   b) handling techniques = 0.00061 kkg/kkg (+30%, -10%)

3) Fraction of methyl chloroform in VOC = 100 percent

4) Vapor Recovery System (MRU) efficiency = 85 percent (±5%)

   a) emissions of methyl chloroform from storage tanks (Vent C)

The uncontrolled and controlled emissions to the air from this source are calculated below:

Uncontrolled Air Emissions = 79,500 kkg x 0.00119 kkg/kkg x 1.00
= 94.6 kkg

Controlled Air Emissions = 94.6 kkg x (1 - 0.85) = 14.2 kkg

The uncertainty of the controlled estimate is +41%, -44%. Vented storage tanks often have refrigeration systems to control diurnal and working losses. The controlled estimate has been included in the multimedia environmental losses of methyl chloroform.

   b) Handling losses (Vent D)

The uncontrolled and controlled emissions to the air due to product handling are calculated below:

Uncontrolled Air Emissions = 79,500 kkg x 0.00061 kkg/kkg x 1.00
= 48.5 kkg

Controlled Air Emissions = 48.5 kkg x (1 - 0.85) = 7.27 kkg

The uncertainty of the controlled estimate is +45%, -37%. Refrigeration of vapors is required for the economic transfer of VOC's. The controlled emission of methyl chloroform due to handling is included in the multimedia environmental losses.

### 2.4.2.4 Emissions to the Air from Other Fugitive Sources Within the Production Plant

Sources of fugitive emissions within the production facilities include process pumps, compressors, process values, and pressure relief devices (Hydroscience, 1979). According to the Hydroscience report, fugitive emissions of methyl chloroform from the vinyl chloride-based production process are estimated at 0.37 g/kg of methyl chloroform also applicable for the vinylidene chloride method, then the fugitive emissions of methyl chloroform can then be calculated using the following assumptions:

1) 1979 production = 79,500 kkg (+0%, -14%)
2) Uncontrolled VOC emission factor = 0.00037 kkg/kkg (±20%)
3) Fraction of methyl chloroform in VOC = 100 percent
4) Emission control efficiency = 90 percent (±5%)

The total uncontrolled fugitive emissions are equal to:

Uncontrolled Air Emissions = 79,500 kkg x 0.00037 kkg/kkg x 1.00 = 29.4 kkg

Assuming that a 90 percent control efficiency could be achieved in fugitive emission sources by the detection and correction of major leaks, the controlled fugitive emission quantity is calculated below:

Controlled Air Emissions = 29.4 kkg x (1 - 0.9) = 2.94 kkg

The uncertainty of this controlled emission quantity is estimated at +54% and -56% due to the following reasons: 1) it is estimated that

100 percent of VOC is methyl chloroform; 2) the variability in leak detections and corrections; and 3) maintenance procedures. The controlled emission estimate is included in the multimedia environmental losses because minimizing fugitive losses improves overall system efficiency.

### 2.4.3 Emissions to Water

Waterborne emission of methyl chloroform discharged by the vinylidene chloride production method is estimated in the range of "ppb" in aqueous effluent waste streams (EPA, 1977a). The quantity of methyl chloroform present in this stream is not mentioned in the study done by MRI (EPA, 1979a).

According to the reported monitoring data near sites of methyl chloroform production (EPA, 1977a), the level of methyl chloroform present in the controlled aqueous effluent of the PPG plant (which produces methyl chloroform by the vinylidene chloride method) ranged from 5 to 180 ppb by weight. We then assume that the weighted composite concentration of methyl chloroform in the controlled aqueous effluent is 120 ppb by weight with an uncertainty of ±50% (EPA, 1977a). Based on the typical daily water discharge of chemical plants of the size of the PPG plant, we estimate that the daily water discharge of this process is 1 million gallons per day. The uncertainty of this figure is ±25%.

Using the above assumptions, the quantity of methyl chloroform emitted to the water in the controlled effluent discharged by vinylidene chloride-based production process can then be calculated by multiplying the following factors:

1) the quantity of water discharged per day = 1 million gallons (±25 percent)

2) the number of operating days per year = 330 days (±5%) (Section 2.2.3)

3) the density of water at 25°C = 1 kg/l

4) the conversion factor from gallon to liter = 3.785 l/gal

5) the concentration of methyl chloroform in the water effluent = 120 ppb (±50%)

Water Emissions =

$$(1{,}000{,}000\ \frac{\text{gal}}{\text{day}})(330\ \frac{\text{days}}{\text{year}})(1\ \frac{\text{kg}}{\text{l}})(\frac{3.785\text{l}}{\text{gal}})(120 \times 10^{-9}\ \frac{\text{kg}}{\text{kg}}) = 150 \text{ kg or } 0.15 \text{ kkg.}$$

Wastewater losses (labeled F in Figure 2.4-1) were identified as a source of VOC emissions by Hydroscience (Hydroscience, 1979). Assumptions used in calculating emissions to water are:

1) 1978 production = 79,500 kkg (+0%, -14%)

2) Uncontrolled VOC emission rate for wastewater treatment = 0.001 kkg/$10^3$ kkg (Hydroscience, 1979) this value was assumed by Hydroscience to be typical of all water discharges during the production of methyl chloroform

3) Fraction of methyl chloroform in VOC (maximum value assumed) = 100 percent

4) No control device used due to low concentrations

The uncontrolled emission of methyl chloroform is:

$$\text{Water Emissions} = 79.5 \times 10^3 \text{ kkg} \times 0.001 \text{ kkg}/10^3 \text{ kkg} \times 1.00$$
$$= 0.0795 \text{ kkg}$$

Assuming the average value from the effluent discharge and Hydroscience calculations, the 1978 emission of methyl chloroform is 0.115 kkg. The uncertainty of this emission is ±31 percent. This assumes the alternative methods for calculating the water emission represents the upper and lower bounds.

### 2.4.3.1 Emission to the Air Due to the Wastewater Treatment

During the wastewater treatment phase, volatile organic compounds (VOC's) such as methyl chloroform, trapped in the aqueous effluent may be emitted to the air due to the aeration process in the treatment system. We assume that 99 percent of the methyl chloroform trapped in the untreated aqueous effluent is released prior to being treated. The remaining 1 percent is treated by the system. Thus, of every 100 parts of methyl chloroform in the aqueous effluent, 99 evaporate prior to water treatment, while the remaining part enters the treatment system. The error of the treated portion is +100%, -50% (Section 2.2.4). Of the 1 percent treated, we assume that 5 percent methyl chloroform is removed during treatment and 95 percent is released intact in the controlled aqueous effluent. The quantity removed from the controlled aqueous effluent is presented with an uncertainty of ±50% (Section 2.2.4). This 95 percent methyl chloroform is represented by the calculated emission to water in the preceding section. Therefore, the total quantity of methyl chloroform emitted to the air from process wastewater can be calculated as follows:

$$(0.115 \text{ kkg}) \left( \frac{100\%}{95\%} \right) \left( \frac{99\%}{1\%} \right) = 12.0 \text{ kkg}$$

Where:

0.115 kkg = the amount of methyl chloroform released to the water by the wastewater treatment system (Section 2.4.3)

100%/95% = the ratio of the percentage of methyl chloroform that enters the treatment system and the untreated percentage discharged into the controlled water effluent (see Section 2.2.4)

99%/1% = the ratio of the percentage of methyl chloroform released to the air prior treatment and the percentage of this chemical that enters the treatment system. (see Section 2.2.4).

The uncertainty of this figure is +106% and -60% due to the uncertainty of the evaporation rate and the removal efficiency of the treatment system. Although the proposed error is large, the estimated upper bound for wastewater treatment air emissions is only 0.04 percent of the methyl chloroform produced by PPG.

### 2.4.4 Emissions to Land

According to the MRI report (EPA, 1979a), a heavy-ends waste stream containing at the maximum of 0.1 percent (or 0.001 kkg/kkg of methyl chloroform produced) of methyl chloroform is discharged by the vinylidene chloride-based production process. It is also reported that this heavy ends waste stream is disposed of in an incinerator (EPA, 1979a).

#### 2.4.4.1 Emission to the Air Due to the Incineration Disposal Method

Information on the incineration disposal method of the heavy end waste stream is not available. We assume that a 95 percent (±4%) destruction of the waste materials is achieved by incineration. The remaining 5 percent is assumed to be emitted to the air during the disposal cycle. We also assume that there is no emission control on the flue gas released by the incinerator. As mentioned above, Midwest Research Institute has estimated that the emission factor of methyl chloroform from the heavy-end waste streams of the vinylidene chloride process is 0.001 kkg/kkg of product (EPA, 1979a). This estimate should be considered as an upper-limit of the calculation of the emission from this source.

Based on the above assumptions, the emission quantity of methyl chloroform to the air from the incinerator can then be calculated using the following assumption:

1) 1978 production = 79,500 kkg (+0%, -14%)

2) uncontrolled emission factor from heavy-end waste stream = 0.001 kkg/kkg

3) fraction of methyl chloroform in VOC = 100 percent

4) the incinerator efficiency = 95 percent (±4%) (Section 2.2.6)

Air Emission = 79,500 kkg x 0.001 kkg/kkg x 100 x (1 - 0.95) = 3.98 kkg

The uncertainty of this value is +80%, -81%.

### 2.4.4.2 Emission to Land

There was no mention in the literature of direct emission of methyl chloroform containing wastes to land (EPA, 1979a; Hydroscience, 1979). We estimate that the amount of methyl chloroform produced from the incinerator ash is not quantifiable.

### 2.4.5 Multimedia Environmental Losses

Figure 2.4-2 shows multimedia environmental losses of methyl chloroform from its production using the vinylidene chloride process. Total multimedia environmental losses are calculated by assuming that PPG uses the appropriate available control technology.

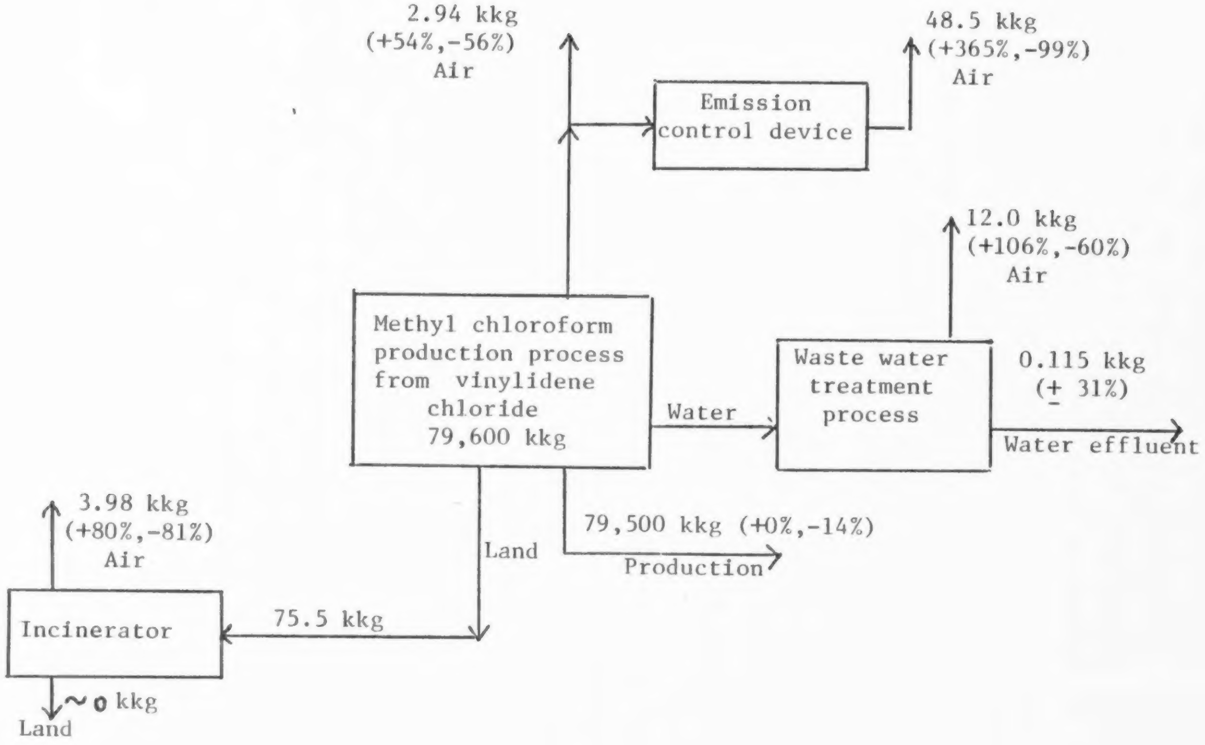

2.94 kkg
(+54%,-56%)
Air
Emission control device
48.5 kkg
(+365%,-99%)
Air
12.0 kkg
(+106%,-60%)
Air
Methyl chloroform production process from vinylidene chloride 79,600 kkg
Water
Waste water treatment process
0.115 kkg
(± 31%)
Water effluent
3.98 kkg
(+80%,-81%)
Air
Land
79,500 kkg (+0%,-14%)
Production
Incinerator
75.5 kkg
~0 kkg
Land

Figure 2.4-2 Multimedia Environmental Losses from the Vinylidene Chloride-based Production Process

## 2.5 INDIRECT PRODUCTION OF METHYL CHLOROFORM BY CHLORINATION

No evidence was found to support the indirect production of methyl chloroform resulting from the chlorination of wastewater or drinking water. The major pathway for the formation of volatile halogenated organics in chlorinated waters is the haloform reaction with humic and fulvic acids. The pattern of this reaction requires the successive replacement of hydrogen by chlorine on a carbon alpha to a carbonyl group followed by hydrolysis to produce $CHX_3$ and a carboxylate (see Figure 2.5-1) (Jolley, 1978). This reaction mechanism does not result in the formation of methyl chloroform.

Analysis of drinking water and treated wastewater before and after chlorination have shown that methyl chloroform concentrations decrease as a result of chlorination, undoubtedly because of evaporative losses.

In one such analysis, secondary treated wastewater from the Metro-Denver treatment plant was analyzed for chlorinated organics before and after chlorination. Chromatograms from headspace analysis of wastewater showed increased concentrations of chloroform; concentrations of trichloroethylene and tetrachloroethylene remained about the same and concentrations of methyl chloroform decreased (Sievers, 1978).

Bellar (Jolley, 1978) analyzed wastewater from several cities before and after chlorination. The results for volatile aliphatic hydrocarbons are summarised in Table 2.5-1. The concentrations of methyl chloroform decreased during the chlorination process (as a result of evaporation) while concentrations of methylene chloride, chloroform, 1,1,2-trichloroethylene and 1,1,2,2-tetrachloroethylene increased as a result of chlorination (Jolley, 1978).

TABLE 2.5-1 - Concentrations of Volatile Chlorinated Organics Before and After Chlorination ($\mu g/l$)

| Compound | Before Treatment | Before Chlorination | After Chlorination |
|---|---|---|---|
| methylene chloride | 8.2 | 2.9 | 3.4 |
| chloroform | 9.3 | 7.1 | 12.1 |
| methyl chloroform | 16.5 | 9.0 | 8.5 |
| 1,1,2,2-tetrachloroethylene | 6.2 | 3.9 | 4.2 |
| 1,2,1-trichloroethylene | 40.4 | 8.6 | 9.8 |

Source: Jolley, 1978

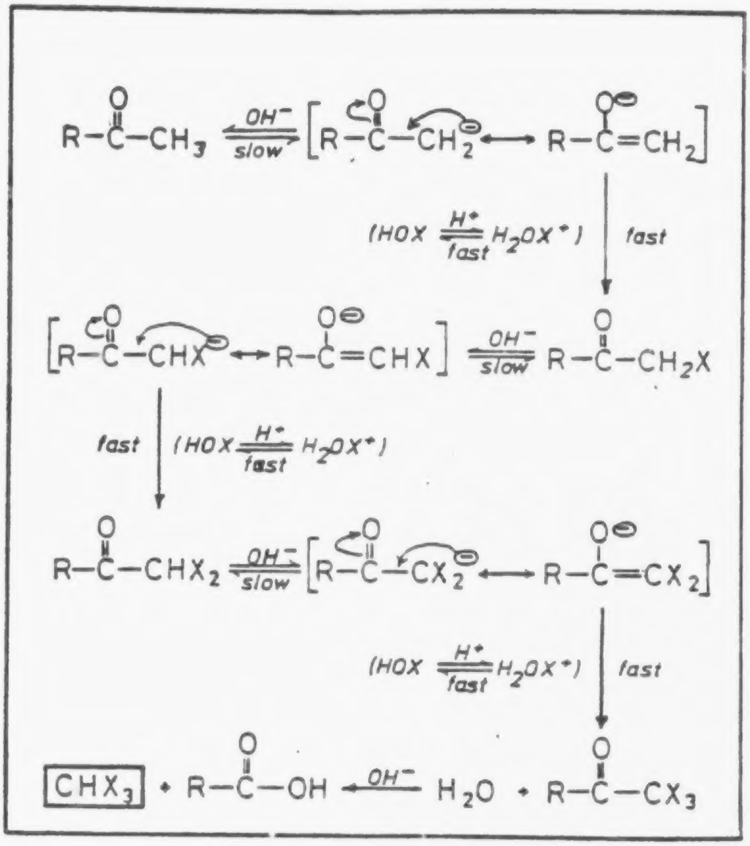


Figure 2.5-1 The Haloform Reaction

Source: Jolley, 1978

## 2.6 PRODUCTION OF METHYL CHLOROFORM FROM NATURAL SOURCES

Information on the production of methyl chloroform from natural sources is not available. We have extensively searched for additional information on this subject, but this information does not exist at all in the literature. Therefore, in this report we assume that the occurrence of methyl chloroform produced from natural sources is very small until future studies indicate differently.

## 2.7 STOCKPILES

### 2.7.1 Introduction

Data for U.S. production and sales of methyl chloroform suggests that various quantities are placed in and retrieved from stockpiles annually. This data is presented in Table 2.7-1.

We assumed that the quantity of methyl chloroform to be added or subtracted from stockpiles was the difference between the total U.S. annual production and the total sales. Internal plant transfers of methyl chloroform for use as a raw material in other processes is not included in the production figures (Woodward, 1979). According to Mr. Woodward of Dow, the methyl chloroform produced (at least by Dow Chemical Company) does not become a raw material for other processes (Woodward, 1979).

### 2.7.2 Quantity Stockpiled

Stockpiles of methyl chloroform are not reported and sales information for 1978 was not available. Therefore, the quantity of methyl chloroform placed-in (retrieved-from) stockpiles must be calculated using historical information.

As presented in Table 2.7-1, the percent of production stockpiled has varied from an 11.8 percent addition to a 4.2 percent reduction. The 10 year average shows a 5.1 percent rate of methyl chloroform added to stockpiles. Between 1972-1975, regulations restricting the use of trichloroethylene in California and other states and market expansion increased the demand for methyl chloroform. Also, in 1975, the Ethyl Corporation closed down their methyl chloroform production plant. These actions produced a shortage of plant capacity and required withdrawals of methyl chloroform from stockpiles. By 1977, the three present manufactures were operating at over 90 percent of their plant capacity (EPA, 1979a) and had new additions under construction. The total 1977 production had exceeded sales by 11.8 percent, thereby providing a new increase to stockpiles.

To estimate the quantity of methyl chloroform stockpiled in 1978, 2- and 10-year averages were used as a likely range. The 1976 and 1977 2-year average provides an upper bound based on an expanding market during heavy U. S. industrial growth. The 10-year average provides a lower bound and represents a long-term market growth trend. 1978 stockpiles are:

$$\frac{7.2\% + 5.1\%}{2} \quad \times 284{,}000 \text{ kkg} = 17{,}500 \text{ kkg}$$

The uncertainty of this number of +10%, -20% due to methyl chloroform market growth, plant additions, and economic health.

The total quantity of methyl chloroform stockpiled between 1966 and 1978 represents approximately a 5 month supply. Economic conditions in 1978 and the length of time required to rebuild a damaged production facility suggest that this may be an optimum quantity in stockpiles.

Table 2.7-1 -- Stockpiles of Methyl Chloroform

| Year | Total Production Quantity kkg | Sales kkg | Stockpile kkg* | Percent of Production Stockpiled |
|---|---|---|---|---|
| 1960-1965 | NA | NA | NA | NA |
| 1966 | 110,179 | 113,263 | (3084) | (2.8%) |
| 1967 | NA | 122,335 | NA | NA |
| 1968 | 135,808 | 130,681 | 5127 | 3.8% |
| 1969 | 147,102 | 135,580 | 11522 | 7.8% |
| 1970 | 166,154 | 148,508 | 17646 | 10.6% |
| 1971 | 169,919 | 154,813 | 15106 | 8.9% |
| 1972 | 199,902 | 176,449 | 23953 | 11.7% |
| 1973 | 248,754 | 256,827 | (8073) | (3.2%) |
| 1974 | 268,350 | 261,136 | 7214 | 2.7% |
| 1975 | 208,112 | 216,912 | (8800) | (4.2%) |
| 1976 | 286,358 | 278,919 | 7439 | 2.6% |
| 1977 | 287,945 | 254,061 | 33,884 | 11.8% |
| 1978 | 284,000 | NA | NA | NA |
| | | | 10 year average | 5.1% |
| | | | 2 year average | 7.2% |

Source: EPA, 1979(a)

*Reductions in stockpile quantity shown in parenthesis ( ).

## 2.8 IMPORTS OF METHYL CHLOROFORM

Information with regard to the importation of methyl chloroform to the U.S. was not available. However, due to surplus quantities (approximately 6 percent of the annual production) and excess U.S. plant capacity present in the industrial sector importation of methyl chloroform is expected to be negligible (EPA, 1979a).

## 3.0 Use and End Products

Methyl chloroform was not used consumptively as an intermediate in the synthesis of any organic chemicals in 1978. Until 1974, about 27,000 kkg methyl chloroform was used in the production of vinylidene chloride but this process is no longer used.

Methyl chloroform is used in several non-consumptive applications which favor the use of chlorinated solvents. The uses and their environmental releases described in this section include:

- Metal cleaning
- Aerosols
- Adhesives
- Textiles
- Drain and septic tank cleaners
- Paints
- Inks
- Catalyst preparations
- Film cleaners
- Pharmaceuticals
- Leather tanning and finishing

The status of methyl chloroform as a solvent for various end-uses is changing as a result of OSHA regulations and existing or potential regulations concerning ozone formation in the troposphere and ozone depletion in the stratosphere. Appendix B discusses the impact of existing or potential regulations on industrial uses of chlorinated solvents.

The assumptions and estimations used to determine environmental losses and destruction of methyl chloroform from various end-uses are detailed in this chapter. Because of the very high evaporation rate of methyl chloroform, any losses to wastewater are assumed to be mostly evaporated before stream discharge. Evaporation of methyl chloroform from land and water disposal are discussed further in Chapter 4.

## 3.1 METAL CLEANING

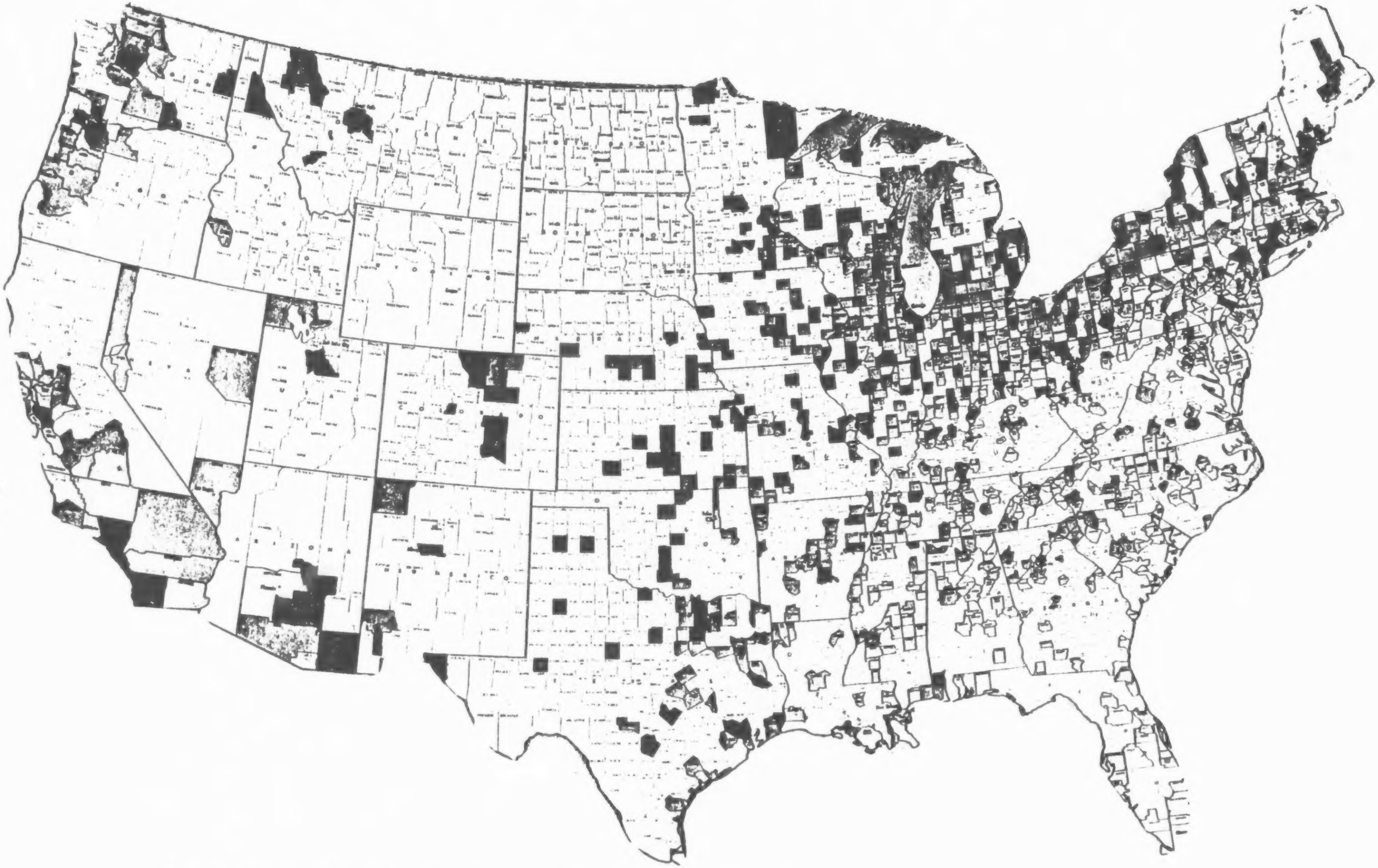
### 3.1.1 Use of Methyl Chloroform in Metal Cleaning

This section quantifies methyl chloroform losses in solvent degreasing operations. Solvent degreasing is widely performed in an estimated 49,000 (±4,600) plants within eight SIC categories included in the metal working industry, (Dow, 1976; Dresser, 1979). Methyl chloroform is commonly used in three applications — manufacturing cold cleaning, open top vapor degreasing, and conveyorized degreasing. Appendix C-1 includes a description of the metal working industry and the major solvent degreasing operations. Solvent degreasers are assumed to be geographically distributed in a manner similar to the metal working industry as a whole. Figure 3.1-1 shows the distribution of metal working plants (Metalworking Data Bank, 1972).

A summary of methyl chloroform materials balance for solvent degreasing operations is shown in Figure 3.1-2. The following discussion details the rationale and calculations for these estimates. Because of the detailed calculations required to estimate losses of methyl chloroform from this industry, many of the calculations have been appendicized.

### 3.1.2 Quantification of Methyl Chloroform Used in Metal Cleaning

Use of methyl chloroform varies with the type of metal cleaning operations. Simple petroleum distillates are the most widely used solvents in cold cleaning operations. Based on EPA data and contacts with an industry selling cold cleaners, 70 to 80 percent of all cold cleaners are used for maintenance operations (EPA, 1977b; G. Pendelton, 1979). There is little opportunity to recover solvents in simple maintenance cold cleaning and consequently less expensive petroleum solvents are generally used. Manufacturing cold cleaners are often required for high quality cleaning. Again, petroleum distillate fractions dominate due to lower cost, but solvent blends with chlorinated solvents and pure chlorinated hydrocarbons, including methyl chloroform, are also used. Vapor degreasing operations use halogenated solvents almost exclusively because they are non-flammable and are much heavier than air. The practice



3.1-1 Geographic Distribution of Metal Working Industry

Source: Metalworking Data Bank

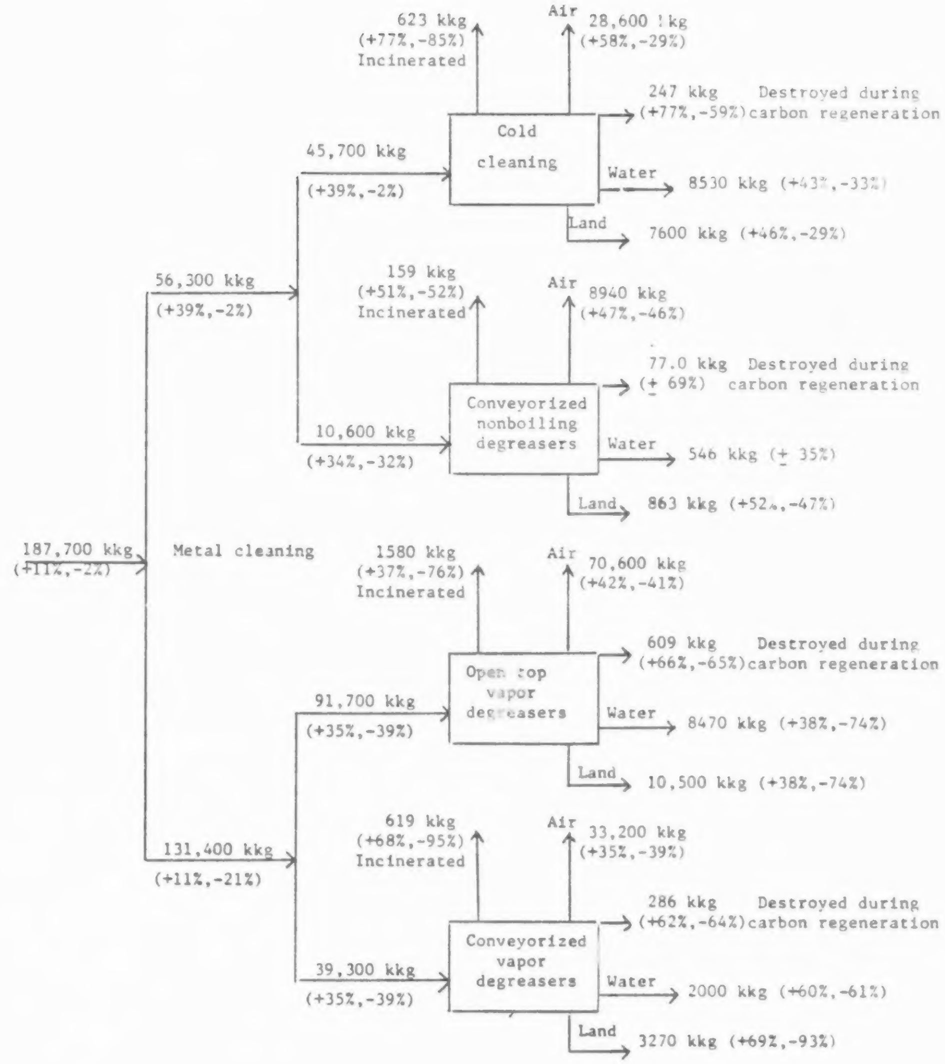

187,700 kkg
(+11%,-2%)
Metal cleaning
56,300 kkg
(+39%,-2%)
45,700 kkg
(+39%,-2%)
Cold cleaning
623 kkg
(+77%,-85%)
Incinerated
Air
28,600 kkg
(+58%,-29%)
247 kkg
(+77%,-59%)
Destroyed during carbon regeneration
Water
8530 kkg (+43%,-33%)
Land
7600 kkg (+46%,-29%)
10,600 kkg
(+34%,-32%)
Conveyorized nonboiling degreasers
159 kkg
(+51%,-52%)
Incinerated
Air
8940 kkg
(+47%,-46%)
77.0 kkg
(± 69%)
Destroyed during carbon regeneration
Water
546 kkg (± 35%)
Land
863 kkg (+52%,-47%)
131,400 kkg
(+11%,-21%)
91,700 kkg
(+35%,-39%)
Open top vapor degreasers
1580 kkg
(+37%,-76%)
Incinerated
Air
70,600 kkg
(+42%,-41%)
609 kkg
(+66%,-65%)
Destroyed during carbon regeneration
Water
8470 kkg (+38%,-74%)
Land
10,500 kkg (+38%,-74%)
39,300 kkg
(+35%,-39%)
Conveyorized vapor degreasers
619 kkg
(+68%,-95%)
Incinerated
Air
33,200 kkg
(+35%,-39%)
286 kkg
(+62%,-64%)
Destroyed during carbon regeneration
Water
2000 kkg (+60%,-61%)
Land
3270 kkg (+69%,-93%)

Figure 3.1-2 Overall Summary of Materials Balance for Methyl Chloroform in Metal Cleaning

of solvent substitution to obtain State Implementation Plan approval has led to the widespread substitution of methyl chloroform for trichloroethylene. Although methyl chloroform is not a perfect substitute for trichloroethylene (methyl chloroform has problems with zinc and aluminum and cannot be applied where there is excessive water) (Rehm, R., GCA, 1979), decreased use of trichloroethylene has led to an increased use of methyl chloroform.

There are several independent estimates of the quantities of methyl chloroform used in degreasing operations from 1974 through 1977. These data have been used to project 1978 estimates. Table 3.1-1 summarizes the estimated use of methyl chloroform in degreasing. Appendix C-1 discusses these and other estimates in further detail.

Table 3.1-1 Estimates of Use of Methyl Chloroform in Solvent Degreasing

| Estimated Consumption of Methyl Chloroform in Solvent Degreasing (kkg/yr) | Year of Estimate | Source of Consumption Estimate | Annual Growth Rate | 1978 Estimate (kkg/yr) | Source of Growth Rate Estimate |
|---|---|---|---|---|---|
| 214,000 | 1976 | EPA, 1979 | 5-7% | 235,935 to 245,009 | SRI (1978); Hugh Farber, Dow Chem. (79) |
| 162,000 (+10%, -0%) | 1974 | QAQPS 1977 | 4% | 189,500 ±10,-0 | Roy George, QAQPS, 1979 |
| 177,000 | 1977 | CEH, (78) Based on EPA Estimate | 5-7% | 186,000 to 189,000 | SRI (1978); Hugh Farber, 1978 |

The 1977 estimate made by SRI was considered the most accurate figure from which to estimate 1978 use, since it is the most recent estimate available. This estimate, ranging from 186,000 kkg to 189,000 kkg, is also consistent with an estimate based on 1974 data from OAQPS, once the annual growth rate was taken into account (EPA, 1977b; George, R. 1979f). Based on other estimates available to OAQPS, the 1974 data is considered accurate to +10% and -0% (See Appendix C-1 for other estimates).

The 1976 estimate of 214,000 kkg was thought to be high because it corresponds to an annual growth rate of 9 to 13 percent from 1974 to 1976. Based on several 1974 estimates shown in Appendix C.1, total methyl chloroform production increased by only 2 percent over the same period (EPA, 1979a).

We estimate that 187,700 kkg of methyl chloroform was used in metal cleaning in 1978. This estimate is considered accurate to +11% and -2% because of the close agreement with the estimate made by OAQPS and to account for the uncertainty suggested by OAQPS data in Appendix C-1.

While the use of methyl chloroform in the metal cleaning industry is estimated to be increasing at 5-7 percent per year, growth is slower in cold cleaning as compared to vapor degreasing. The number of cold cleaning operations has increased from 122 million units in 1974 (EPA, 1977b) to 135 million units in 1978 (SRI, 1978). This corresponds to approximately 3 percent growth per year. Seventy to eighty percent of the cold cleaning operations are maintenance cleaners which rarely use methyl chloroform or other halogenated solvents (Pendelton, G. 1979; EPA, 1977b). Approximately 30 million cold cleaners are manufacturing units, which are more likely to use halogenated solvents. In contrast, the number of open top vapor degreasers (32,000) (SRI, 1978) increased at a rate of 10 percent annually since 1974 when 22,000 units were reported (EPA, 1977b). A growth rate of only about 5 percent was projected for vapor degreasers between 1976 and 1980 (EPA, 1979f).

Efforts were made to determine how much of the 187,700 kkg of methyl chloroform consumed in metal cleaning operations was used for cold cleaning and how much was used in vapor degreasing. Contacts were made to methyl chloroform producers and manufacturers of metal cleaning equipment. Many of the contacts indicated that they were only "guessing" or that the split between vapor degreasers and cold cleaners was difficult to determine. Under these circumstances it was decided to use the results of the Dow survey of solvent metal cleaning operations conducted in 1974 to estimate the respective quantities of methyl chloroform used by cold cleaners and vapor degreasers. The results of the survey were used and adjusted to account for the growth rate of cold cleaning and vapor degreasing units and the effect of solvent substitution for trichloroethylene.

The results of the Dow Survey suggested that in 1974, 36 percent of the methyl chloroform consumed in metal cleaning was used for cold cleaning and 64 percent was used for vapor degreasing. Accounting for a growth rate of 3 percent and 10 percent for cold cleaning and vapor degreasing, respectively and for the effects of solvent substitution, JRB estimates that 30 percent of the methyl chloroform was used in cold cleaning and 70 percent in vapor degreasing. In accounting for the growth rate it was necessary to assume that use of methyl chloroform increased in proportion to the increased number of units. Appendix C-2 details the calculations used to determine this split. Based on this distribution, the quantity of methyl chloroform used in cold cleaning and vapor degreasing is determined as follows:

Cold Cleaning:

| Total Methyl Chloroform Used in Metal Cleaning | Percent of Total Used in Cold Cleaning | | Total Used in Cold Cleaning |
|---|---|---|---|
| | | = | |
| (187,700 kkg) | (0.3) | = | 56,300 kkg |

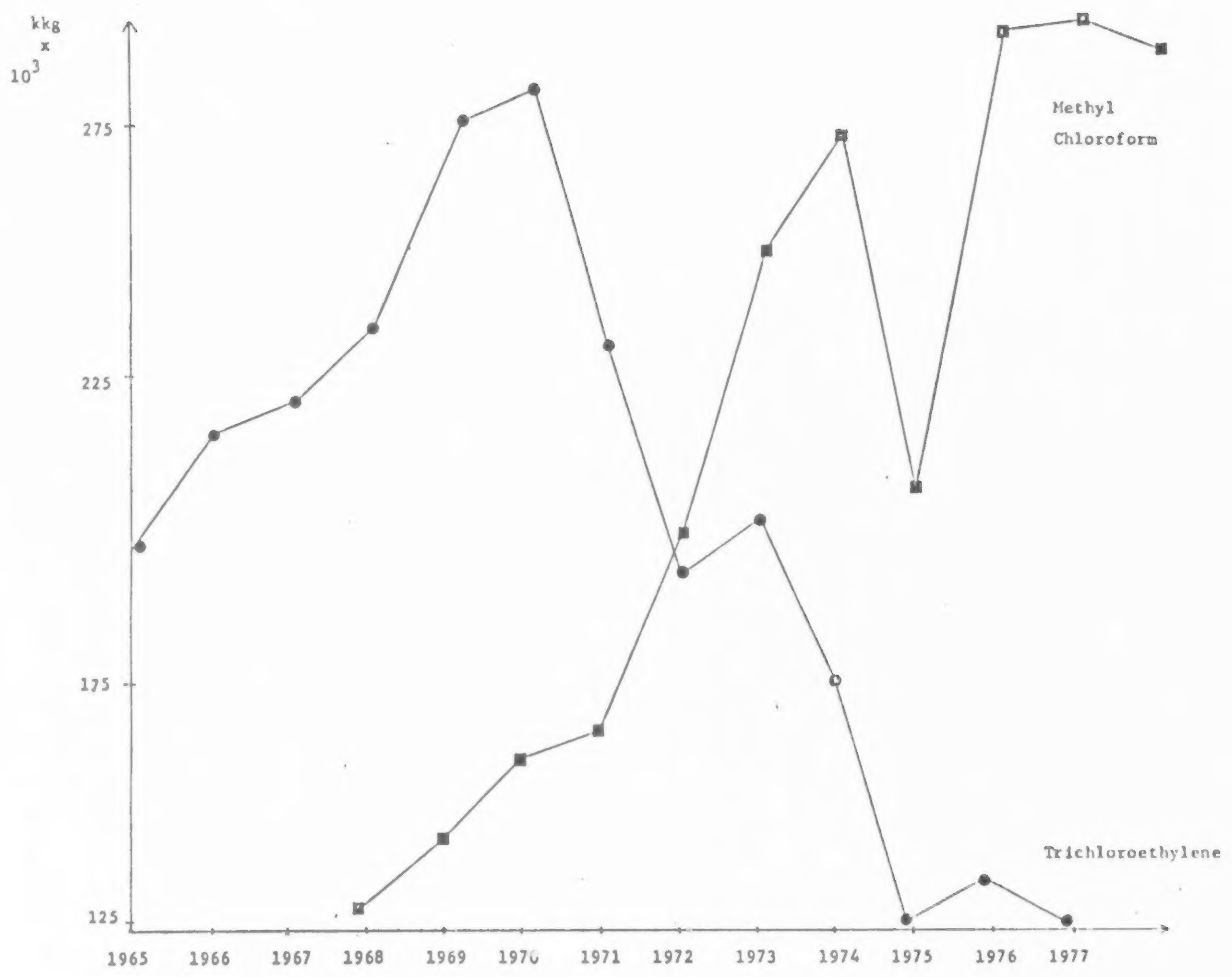


Figure 3.1-3 Production Trends for Methyl Chloroform and Trichloroethylene

Vapor Degreasing:

| Total Methyl Chloroform Used in Metal Cleaning | Percent of Total Used in Vapor Degreasing | = | Total Used Vapor Degreasing |
|---|---|---|---|
| (187,700 kkg) | (0.7) | = | 131,400 kkg |

The decision to use the results of the Dow survey as a basis for determining the split between cold cleaning and vapor degreasing was based on the following factors:

- The Dow survey results were the only actual survey results available.
- Although the survey was based on users with 20 employees or more, these results are probably representative for methyl chloroform. The high cost of this solvent precludes its use among many small operations.
- The results of the estimate based on the Dow survey are in good agreement with estimates being used by GCA Technology, a contractor for the OAQPS. GCA estimates that one-third of the methyl chloroform was used in cold cleaning and two-thirds was used for vapor degreasing the Dow survey, was also the basis for this estimate (Rehm, R., GCA, 1979).
- Finally Mansanto estimated that in 1974, 45 percent of the methyl chloroform was used for cold cleaning and 35 percent for vapor degreasing (EPA, 1977b). Accounting for solvent substitution and the growth rate, approximately 39 percent and 61 percent would have been used for cold cleaning and vapor degreasing in 1978. This estimate is in reasonably good agreement with our estimate, based on the Dow survey.

Detrex estimated the split at 59 percent and 41 percent for vapor degreasing and cold cleaning, respectively (MRI, 1979). This estimate of percent distribution differs most significantly from the JRB estimate.

If Detrex's estimate is more representative of methyl chloroform usage, JRB's estimate of 56,300 kkg for cold cleaning may be low by 37 percent and the estimate of 131,400 kkg for vapor degreasing may be high by 21 percent. Accounting for an uncertainty estimate of +11% and -2% for the total methyl chloroform used in metal cleaning, our overall uncertainty estimates are +39% and -2% for cold cleaning and +11% and -21% for vapor degreasing.

### 3.1.3 Emissions from Cold Cleaning Operations

#### 3.1.3.1 Sources of Emissions From Cold Cleaning Operations

Figure 3.1.-4 shows points of emission from a typical cold cleaning operation.

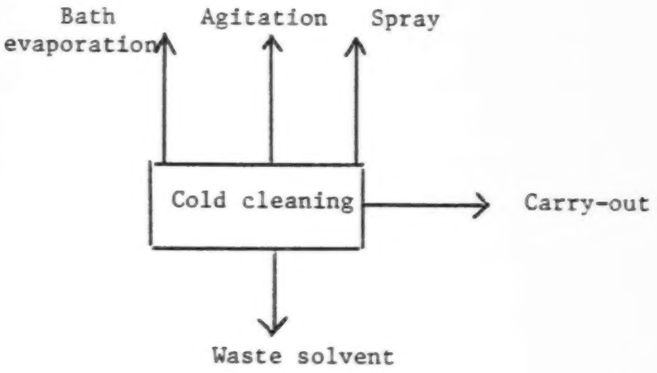


Figure 3.1-4 Points of Emission from a Cold Cleaning Operation

Waste solvent may contribute 40 to 60 percent of total solvent evaporative losses where reclamation is not practiced (EPA, 1977b). Operations using halogenated solvents are more likely to recover waste solvent because of the high cost of chlorinated solvents (EPA, 1977b). It is often the case, however, that methyl chloroform is used in mixtures with less costly solvents. It was estimated that at the time of the Dow survey in 1974 that only about 20 percent of cold cleaning operations were recycling solvents; but this practice has been steadily increasing (Richards, D., Dow 1979). The National Solid Waste Management Association estimated that 30 - 40 percent of the solvent used in cold cleaning is reclaimed (NSWM, 1980). JRB assumes that 30 percent of the methyl chloroform was reclaimed in 1978. The remaining waste solvent is disposed of by flushing, landfilling or incineration.

Depending upon control practices, evaporative losses from spray and agitation and losses from carry out are highly variable. For highly volatile solvents, such as methyl chloroform, room ventilation and use of a cover are the most critical factors in determining solvent losses from evaporation.

Table 3.1-2 summarizes the major control variables influencing solvent losses.

Table 3.1-2 Major Control Variables for Cold Cleaners

| Loss | | Control |
|---|---|---|
| Evaporation | o | Room ventilation |
| | o | Surface area of the tank |
| | o | Use of cover; manual vs. automatic |
| | o | Freeboard height |
| | o | Use of carbon adsorption |
| Carry-out | o | Racks for draining parts |
| | o | Use of internal drainage |
| | o | Time allotted for drainage |
| Waste-Solvent | o | Reclamation practices |

Because of the variability in emission controls and in the type of metal cleaning application, there is no "typical" cold cleaner nor "typical" annual emission rate. Table 3.1-3 shows results of several test runs using cold cleaners, with and without various controls. The results clearly indicate the wide variability in solvent losses depending upon the controls used and the type of equipment.

Figure 3.1-3 Efficiencies of Control Options in Controlling Solvent Losses From Cold Cleaners

| Unit | Surface Area | Control | Emissions Without Control | With Control | Percent Control Efficiency | Solvent | Comment |
|---|---|---|---|---|---|---|---|
| Kleer-Flo Model 90 | $m^2$<br>0.97 | Air Draft Decreased from 85m/min to 27m/min | $\frac{kkg/hr/m^2}{(kkg/yr)^*}$<br>2.8<br>(11.2) | $\frac{kg/hr/m^2}{(kkg/yr)^*}$<br>1.0<br>(4.0) | 64% | Perechloro-ethylene | Evaporation Losses Only |
| Kleer-Flo<br>Model 90 | 0.97 | Cover | 2.8<br>(11.2) | 0.2<br>(0.8) | 93% | Perechloro-ethylene | Air Draft Maintained at 83-85m/min Evaporation Losses Only |
| Gray Mills SL-32 | 0.33 | Increased Freeboard 0.27-0.50 | 1.2<br>(5.8) | 0.8<br>(3.2) | 34% | Perechloro-ethylene | Air Draft 52-57m/min Evaporation Losses Only |
| Baron Blakeslee HD425 (operated in cold mode) | 1.1 | Solvent Reclamation | 0.14<br>(.16) | 0.04<br>(.16) | 70% | 1.1.1 Trichloro-ethane | Waste Solvent Losses Only |

*Based on 250 day/yr; 16 hr/day.

Source: Dow, 1976

## Emissions of Methyl Chloroform from Cold Cleaning

Total emissions from cold cleaning operations were estimated in Section 3.1.1 to be 56,300 kkg. This estimate includes losses from non-boiling conveyorized degreasers which are considered in section 3.1.2.4. Total losses from conveyorized non-boiling degreasers have been estimated at 10,600 kkg based upon the assumptions discussed in Appendix C-3. Total losses from all other cold cleaners are estimated as follows:

|  |  |  |  |  |
|---|---|---|---|---|
| Total Cold Cleaning Losses | - | Losses from Non-Boiling Conveyorized Degreasers | = | Losses from Non Conveyorized Cold Cleaners |
| (56,300 kkg) | - | (10,600 kkg) | = | 45,700 kkg |

Although emission rates vary widely, annual average emissions have been estimated for the study. We assumed there were 1.35 X $10^6$ cold cleaners in 1978 and 30 percent of these are manufacturing units; which are more likely to use halogenated solvents (EPA, 1977b). Based on the Dow survey, we estimate that 18 percent of the manufacturing cold cleaners use methyl chloroform (Dow, 1976). The total number of cold cleaning units using methyl chloroform is estimated as follows:

|  |  |  |  |  |
|---|---|---|---|---|
| Total Number of Cold Cleaners | Percent Which are Manufacturing Units | Percent Using Methyl Chloroform | = | Total Number of Cold Cleaners Using Methyl Chloroform |
| (1.35 x $10^6$) | (0.3) | (0.18) | = | 72,900 units |

Emissions per unit are estimated by dividing the total methyl chloroform used by the number of units.

45,700 kkg/72,900 units = 0.63 kkg/unit

Using JRB derived estimates, annual emissions approximate 0.63 kkg/unit. The OAQPS has estimated typical emissions from a manufacturing cold cleaner at 0.5 kkg/unit (EPA, 1977b). This emission rate, however, was based on an average for all solvents, not only methyl chloroform. JRB's estimate of 0.63 kkg/unit/yr is within 20 percent of the estimate made by OAQPS (EPA, 1977b).

Total methyl chloroform emissions to air, water and land are shown in Figure 3.1-5.

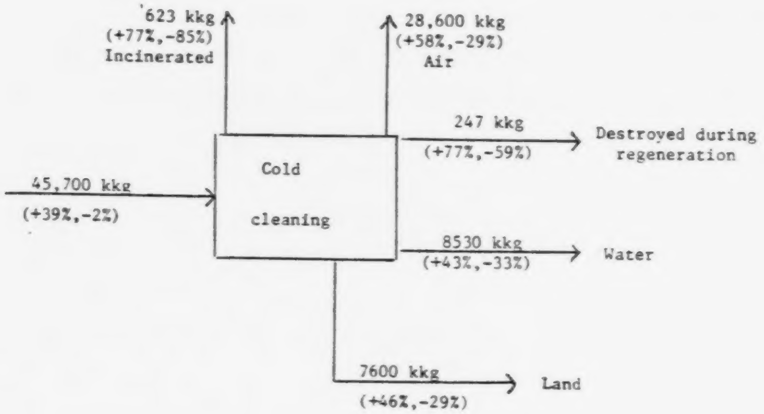

623 kkg
(+77%,-85%)
Incinerated
28,600 kkg
(+58%,-29%)
Air
247 kkg
(+77%,-59%)
Destroyed during regeneration
45,700 kkg
(+39%,-2%)
Cold cleaning
8530 kkg
(+43%,-33%)
Water
7600 kkg
(+46%,-29%)
Land

Figure 3.1-5 Multimedia Environmental Losses of Methyl Chloroform from Cold Cleaning*

*Numbers may not add due to rounding

Losses were calculated for the 72,900 cold cleaning units which used 45,700 kkg methyl chloroform in 1978.

Detailed calculations for these emissions are presented in Appendix C-4. The assumptions used to calculate these multimedia environmental releases are:

- Solvent Reclamation

  JRB estimated that 30 percent of the methyl chloroform is reclaimed at 90 percent efficiency. Although solvent recovery services are more efficient in reclaiming solvent, many of the operations are equipped with their own stills which operate at lower efficiency. It was also assumed that 25 percent of the still bottoms (172 kkg) were incinerated at 95 percent efficiency and the remaining 75 percent (517 kkg) were landfilled. Although some reclamation services incinerate all the still bottoms (Solvent Recovery Service of the Northeast, 1979) there are currently very few approved incinerators for chlorinated hydrocarbons.

- Waste Solvent:

The remaining 70 percent of the waste solvent (16,100 kkg) was disposed of by landfilling, flushing or by incineration. The Dow survey suggested that unreclaimed waste solvent was disposed of as follows:

| | | |
|---|---|---|
| o | Incineration | 3 percent (±5%) |
| o | Landfilling | 44 percent (+15%, -5%) |
| o | Flushing | 53 percent (+5%, -15%) |

Although several contacts were made in an effort to update this information, no reliable estimates were obtained. One large manufacturer of metal cleaning equipment indicated that most of his clients landfilled their solvent, although flushing was also common. An Effluent Guidelines Survey of the metal cleaning industry suggested that 79 percent of the plants discharged waste solvent to the sewer and only 21 percent, landfilled the waste (Dresser, 1979). However, the number of operations surveyed and made available to JRB was too small to generalize from (only 14 plants).

Atmospheric Losses:

Direct atmospheric emissions from bath evaporation, agitation, spray and carry-out were estimated to be the difference between the total solvent losses from cold cleaning and the waste solvent losses.

| Total Methyl Chloroform Losses from Cold Cleaning | - | Losses from Still Bottoms | + | Waste Solvent Losses | = | Total Atmospheric Emissions |
|---|---|---|---|---|---|---|
| (45,700 kkg) | - | (16,100 kkg | + | 689 kkg) | = | 28,900 kkg |

Only about 1.5 percent of the operations use activated carbon to recover atmospheric losses and the efficiency of recovery is about 60 percent (Dow, 1976). As Appendix C-4 indicates this practice reduces direct atmospheric losses by about 260 kkg to 28,600 kkg.

As Figure 3.1-5 indicates 63 percent of the solvent is emitted directly to the air. Approximately 2 percent of the solvent is destroyed during incineration or carbon regeneration and 16 percent of the waste solvent was determined to be landfilled. No information was available on the quantities of landfilled wastes that are properly containerized and air emissions from land disposal of waste solvent cannot be estimated. The remaining 19 percent of the solvent is discharged, mainly to municipal treatment systems. It is assumed that 95 percent of the methyl chloroform (8100 kkg) evaporates before stream discharge.

The overall uncertainties for the estimates of multimedia releases must account for uncertainties related to: (1) the total quantity of methyl chloroform used in metal cleaning (187,700, +11% and -2%); (2) the quantity used in cold cleaning verses vapor degreasing (56,300 kkg, +39% and -2%; (3) the quantity of unreclaimed waste solvent generated and the means of disposal of the waste solvent (Appendix C-4); and (4) the quantity of still bottoms generated and the means of disposal (Appendix C-4). The estimated overall uncertainty factors for the quantities shown in Figure 3.1-5 based on the above individual uncertainties are +43 and -33 percent for water, +46 and -29 percent for land, +77 and -85 percent for the quantity incinerated and +58 and -29 percent for emissions to air.

The major factor contributing to these large uncertainties is the uncertainty related to the amount of methyl chloroform used in cold cleaning as compared to vapor degreasing.

Figure 3.1-6 shows the geographic distribution of cold cleaning operations based on Dow survey (1976) and the total annual emissions for each geographic area. Control technologies were assumed to be similar for each geographic area. Emissions are largely concentrated in the northeast and midwest where 65 percent of all cold cleaning operations are located.

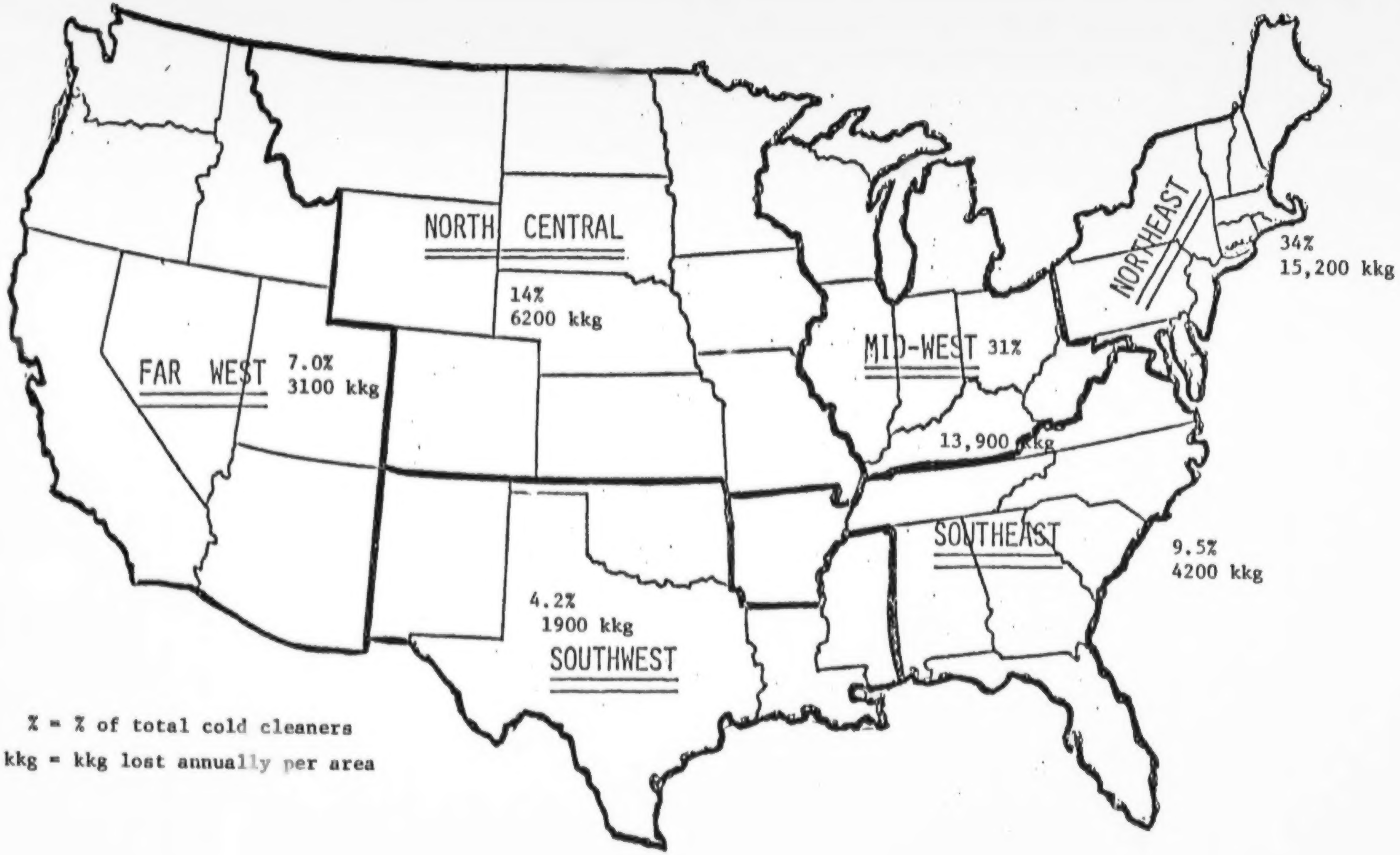

NORTH CENTRAL
14%
6200 kkg
FAR WEST
7.0%
3100 kkg
MID-WEST 31%
13,900 kkg
NORTHEAST
34%
15,200 kkg
SOUTHEAST
9.5%
4200 kkg
4.2%
1900 kkg
SOUTHWEST
% = % of total cold cleaners
kkg = kkg lost annually per area

Figure 3.1-6 Geographic Distribution of Methyl Chloroform from Cold Cleaning

### 3.1.4 Emissions from Open Top Vapor Degreasers

It was estimated in Section 3.1.1 that 131,000 kkg methyl chloroform were lost in 1978 from the operation of vaporized degreasers. Seventy percent of these losses are attributable to open top vapor degreasers (OTVD) and 30 percent to conveyorized vapor degreasers (CVD).

(131,000 kkg) (0.7) = 91,600 kkg from OTVD

(131,000 kkg) (0.3) = 39,300 kkg from CVD

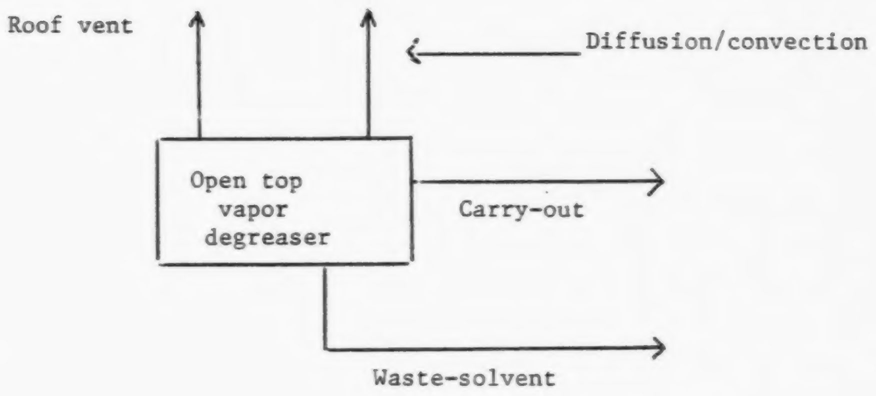


Figure 3.1-7 Points of Emission from an Open Top Vapor Degreaser

This section deals with emissions from OTVD only. Figure 3.1-7 shows points of emission from an OTVD. Solvent reclamation is much more widely practiced for OTVD operations than for cold cleaning. Because of better waste solvent control practices, a smaller proportion of the solvent losses are due to waste solvent and liquid carry-out. Most of the emissions are those which diffuse out of the degreaser.

Table 3.1-4 summarizes the major control variables influencing solvent losses by diffusion and convection and the percent control efficiency observed under test runs. The extent to which some control practices are used is not well know. It is known, however, that most vapor degreasers do recycle waste solvent. As indicated previously, the results of the Effluent Guidelines Survey for Mechanical Products found that 73 percent of solvent degreasing operations recovered waste solvent (Dresser survey, 1979). A contact with Phillips Incorporated indicated that approximately 75 percent of all vapor degreasers are equipped with stills (Raquat, D., 1979). This estimate was also in agreement with an estimate made by NSWMA (1980). It is estimated that about 1.5 percent of all open top vapor degreasers use activated carbon and 12 percent are equipped with refrigerated chillers (Dow, 1976; Raquat, D. 1979). The extent to which covers are used to control emissions is not known. Open top vapor degreasers range in size from a table-top model with dimensions of 0.3m x 0.6m up to degreasers which are 36m long and 2m wide. Because of the wide variability in sizes of degreasers and in the types of solvent control options, there are no typical units nor typical emission rates.

Emissions from OTVD

The number of OTVD which use methyl chloroform was estimated from the Dow Survey and adjusted for solvent substitution (Dow, 1976). Using this data, an estimated 30 percent of the 32,000 OTVD use methyl chloroform.

| Number of OTVD | Percent Using Methyl Chloroform | = | Total Number of Units Using |
|---|---|---|---|
| (32,000 units) | (30) | = | 9,600 units |

The average unit loss of methyl chloroform is estimated from the following expression.

$$\frac{\text{Total Methyl Chloroform Losses from OTVD}}{[\text{No. of OTVD}]} = \text{Average Annual Loss Per Unit}$$

$$\frac{91{,}700}{9{,}600}\text{ kkg} = 9.55 \text{ kkg/unit}$$

Table 3.1-4 Control Variables - Open Top Vapor Degreasers

| Control | Solvent Losses No Control | Solvent Losses with Control | Percent Efficiency | Surface Area | Surface Used | Type Degreaser |
|---|---|---|---|---|---|---|
| | kg/m$^2$/hr | kg/m$^2$/hr | | m$^2$ | | |
| Cover | 1.72 | 0.91 | 47% | 1.67/ 1.2 | Methylene Chloride | Crest Ultrasonics |
| Regrigerated Freeboard Chiller | 1.72 | 1.24 | 28% | 1.2 | Methylene Chloride | Crest Ultrasonics |
| Refrigerated Freeboard Chiller and Cover | 1.72 | 0.55 | 60% | 1.67/ 1.2 | Methlene Chloride | Crest Ultrasoncis |
| Pneumatic Cover | 0.78 | 0.49 | 37% | 5.3 | Methyl Chloroform | Detrex DUS-800-S |
| Regfigerated Freeboard Chiller and Cover | 0.67 | 0.57 | 15% | 3.8 | Methyl Chloroform | Detrex DUS-800-S |
| Carbon Adsorption | 2.9 | 1.05 | 65% | 5.9 | Trichloroethylene | Blakeslee D-95-9 |
| Freeboard Height (quiet air) | 0.46<br>(.5) = ratio | 0.25<br>(.75) = ratio | 46% | 0.4 | Methyl chloroform | Detrex 2D500-E |

This estimate is in good agreement with an estimate made by OAQPS that an average of 9.5 kkg solvent are emitted from uncontrolled OTVD.

Total methyl chloroform losses to air, water and land are summarized in Figure 3-8. Detailed calculations for these estimates are included in Appendix C-5.

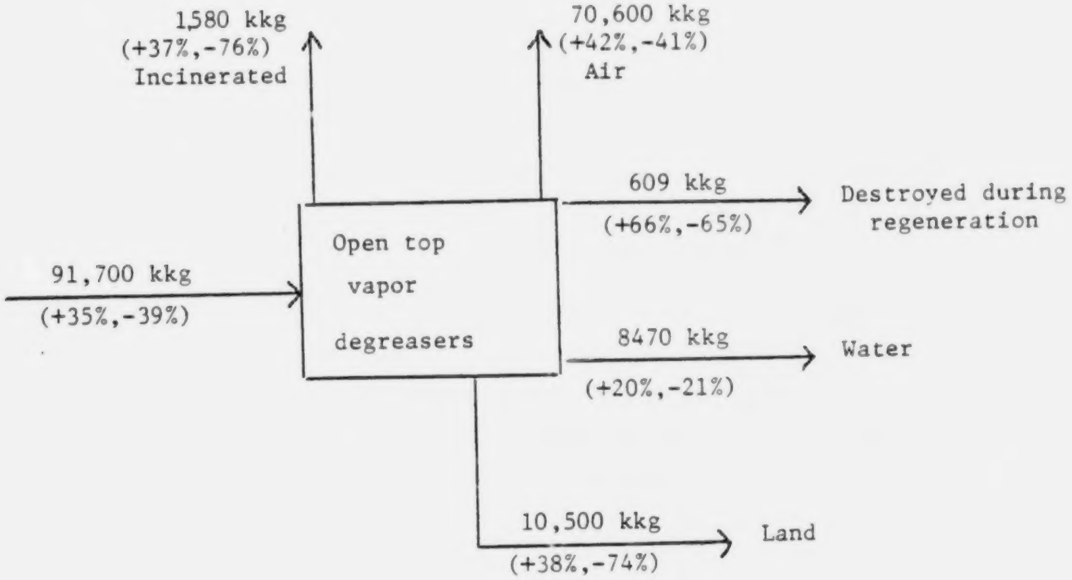

1,580 kkg
(+37%,-76%)
Incinerated
70,600 kkg
(+42%,-41%)
Air
609 kkg
(+66%,-65%)
Destroyed during regeneration
91,700 kkg
(+35%,-39%)
Open top vapor degreasers
8470 kkg
(+20%,-21%)
Water
10,500 kkg
(+38%,-74%)
Land

Figure 3.1-8 Multimedia Environmental Losses of Methyl Chloroform from Open Top Vapor Degreasers*

*Numbers may not add due to rounding

Losses were estimated for 9,600 OTVD units which emitted a total of 91,700 kkg methyl chloroform in 1978 or 9.55 kkg per unit.

In order to derive the estimates for multimedia releases shown in Figure 3.1-8, the following assumptions were made:

### 1) Still Bottoms

It has been estimated that 20-25 percent of the total virgin solvent becomes waste solvent in OTVD operations (EPA, 1977b). The estimated 20,600 kkg waste solvent includes both still bottoms and unreclaimed waste solvent. Based on information from the Effluent Guidelines Survey, the NSWMA, and from Phillips, Inc, an estimated 75 percent of the OTVD operations are equipped with distillation equipment for solvent recovery (EPA, 1979; NSWMA, 1980; Raquat, D., 1979). Methyl chloroform losses in still bottoms, 4750 kkg, were estimated by assuming that 75 percent of the solvent is reclaimed at 90 percent efficiency. The disposal of still bottoms was assumed to be the same as for cold cleaning operations; 25 percent are incinerated and 75 percent are landfilled.

### 2) Unreclaimed Waste Solvent

The quantity of unreclaimed still bottoms (15,800 kkg) was estimated by assuming that 25 percent of the operations do not practice solvent recovery. The disposal of unreclaimed waste solvent was assumed to be the same as for cold cleaning; 3 percent was incinerated, 44 percent was landfilled and 53 percent was flushed. These estimates were based on the Dow Survey (Dow, 1976)

### 3) Direct Atmospheric Losses

Direct atmospheric emissions, determined to be 70,500 kkg, were estimated as the difference between total losses from OTVD and losses from waste solvent.

| Total Methyl Chloroform Losses | | Unreclaimed Waste Solvent | | Still Bottoms | | Total Atmospheric Emissions |
|---|---|---|---|---|---|---|
| (91,700 kkg) | - | (15,800 kkg | + | 4750 kkg) | = | 71,200 kkg |

This quantity was then adjusted to account for an estimated 1.5 percent of the operations using carbon adsorption of about 60 percent efficiency. (Dow, 1976). The practice of using carbon adsorption reduced emissions by 641 kkg and actual atmospheric losses were estimated at 70,500 kkg.

Figure 3.1-8 indicates that approximately 77 percent of the annual methyl chloroform used in open top vapor degreasers is emitted directly to the atmosphere. An estimated 9 percent is discharged to municipal treatment systems and approximately 8000 kkg of this quantity or 95 percent reaches the atmosphere by evaporation before stream discharge. Approximately 11 percent of the solvent is disposed of to land. No information was available on how these wastes are containerized and therefore no estimate of air emissions can be made. The remaining 3 percent of the solvent was incinerated or destroyed during activated carbon regeneration.

The overall uncertainties for the quantities shown in Figure 3.1-8 are a function of the following individual uncertainties:

1) The total quantity of methyl chloroform used in solvent degreasing (187,700 kkg, +11% and -2%)

2) The total methyl chloroform used for vapor degreasing (131,400 kkg, +11% and -21%)

3) Uncertainties related to the quantities of still bottoms generated and the final disposal methods for the still bottoms (see Appendix C-5)

4) Uncertainties related to the quantities of unreclaimed waste solvent generated and the final disposal of the waste solvent (see Appendix C-5)

5) Uncertainty related to air emissions (70,500 kkg, +42/-41 percent)

Based on these individual uncertainties our overall uncertainty estimates are: +42 and -41 percent for releases to air; +20 and -21 percent for the quantity discharged; +38 and -74 percent for the quantity released to land, +37 and -76 percent for the quantity incinerated and +66 and -65 percent for the quantity destroyed during carbon regeneration.

Figure 3.1-9 shows the percent distribution of open top vapor degreasers in various geographic regions and the corresponding methyl chloroform losses (Dow, 1976). Methyl chloroform losses are estimated by assuming control technology and disposal techniques are similar throughout all geographic regions.

### 3.1.5 Emissions from Conveyorized Vapor Degreasers

There are an estimated 5,000 conveyorized degreasers, 85 percent of which are vapor degreasers (EPA, 1977b). Based on the Dow survey (1976), it is assumed that 30 percent use methyl chloroform. Solvent emissions from conveyorized vapor degreasers are similar in source to those described for open top degreasers. However, enclosures common for these degreasers reduce emisssions from natural air drafts or fans. Also, the conveyorized design usually eliminates most poorer degreaser operations and major drag out sources. Although conveyorized degreasers emit more methyl chloroform than do OTVD or cold cleaners, they actually emit less solvent per part cleaned.

Annual emissions to air, water and land are shown in Figure 3.1-10. Detailed calculations are included in Appendix C-6. Estimates were made assuming 1,280 conveyorized vapor degreasers and annual methyl chloroform losses of 39,300 kkg. It was assumed that 85 percent of conveyorized vaporized degreasers practiced solvent recovery. All other estimates were the same as those made in determining losses from vapor degreasing.

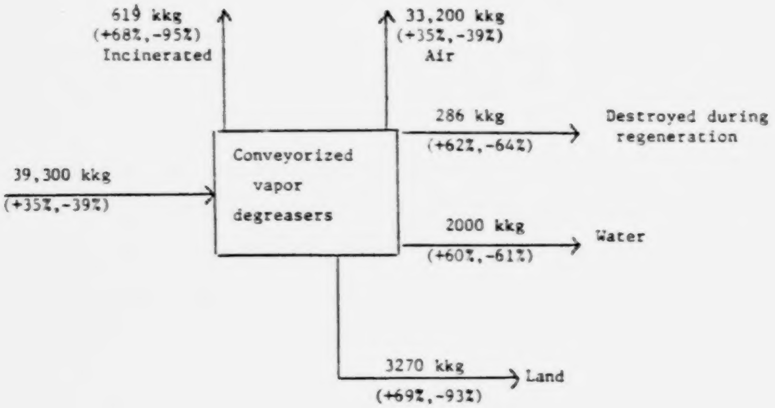


Figure 3.1-10 Multimedia Environmental Losses of Methyl Chloroform from Conveyorized Vapor Degreasers*

*Numbers may not add due to rounding

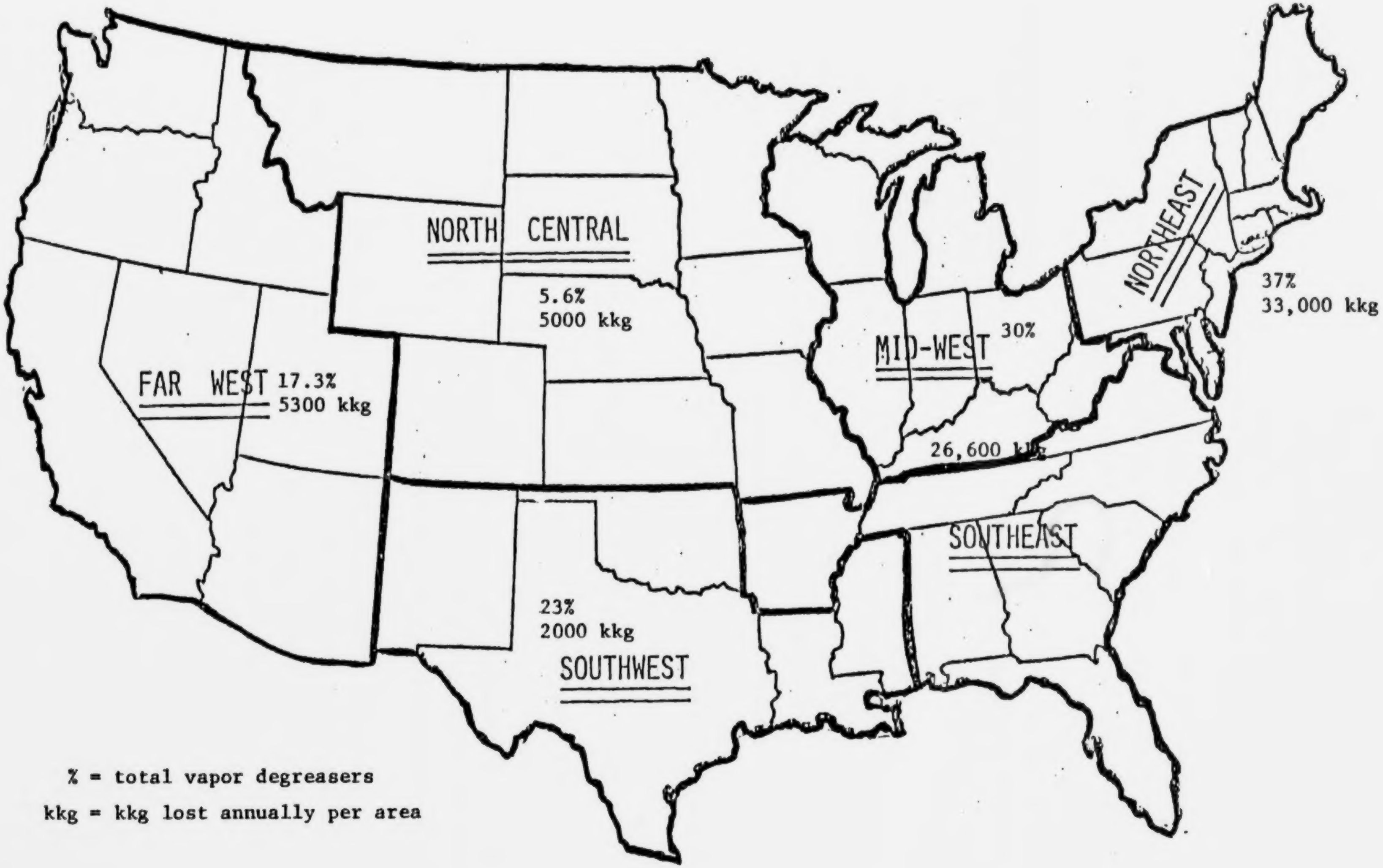

NORTHEAST
37%
33,000 kkg
NORTH CENTRAL
5.6%
5000 kkg
MID-WEST 30%
26,600 kkg
FAR WEST 17.3%
5300 kkg
SOUTHEAST
23%
2000 kkg
SOUTHWEST
% = total vapor degreasers
kkg = kkg lost annually per area

Figure 3.1-9 Geographic Distribution of Methyl Chloroform Losses from Vapor Degreasing

Because solvent recovery is widely practiced in the operation of conveyorized degreasing, waste solvent is minimal and most of the solvent losses are directly to the atmosphere.

Figure 3.1-10 indicates that 84 percent of the methyl chloroform was emitted to air, less than 3 percent was destroyed by incineration or during carbon regeneration, 5 percent was discharged and about 8 percent was landfilled. It was assumed that 95 percent of the quantity discharged (1900 kkg) was emitted to air before stream discharge. No estimate was made for releases to air from landfilled waste solvent.

As was indicated for cold cleaners and vapor degreasers, the overall uncertainty estimates are a function of several individual uncertainties. Accounting for these individual uncertainties, overall uncertainties are as follows: +60 and -61 for the quantity discharged; +69 and -93 for the quantity landfilled; +68 and -95 percent for the quantity incinerated; +35 and -39 percent for the quantity released directly to air and +62 and -64 percent for the quantity destroyed during carbon regeneration.

### 3.1.6 Emissions from Conveyorized Non-boiling Degreasers

Non-boiling degreasers are not designed to prevent solvent losses as adequately as conveyorized vapor degreasers. OAQPS estimated that a typical non-boiling conveyorized degreaser, (CND) loses nearly twice as much solvent as a conveyorized vapor degreaser. (EPA, 1977b) Points of emission are the same as from OTVD.

Figure 3.1-11 shows annual losses of methyl chloroform from non-boiling conveyorized degreasers. Losses were calculated based on 225 units with total annual losses of 10,600 kkg or 47 kkg per unit (see Appendix C-7 for detailed calculations).

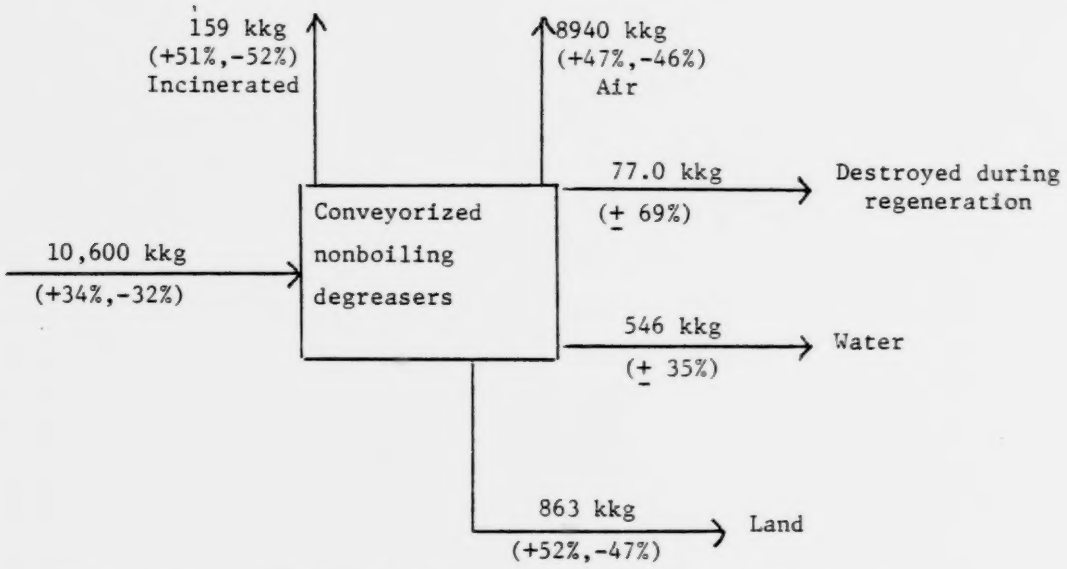

159 kkg
(+51%,-52%)
Incinerated
8940 kkg
(+47%,-46%)
Air
77.0 kkg
(± 69%)
Destroyed during regeneration
10,600 kkg
(+34%,-32%)
Conveyorized nonboiling degreasers
546 kkg
(± 35%)
Water
863 kkg
(+52%,-47%)
Land

Figure 3.1-11 Multimedia Environmental Losses of Methyl Chloroform from Conveyorized Nonboiling Degreasers*

*Numbers may not add due to rounding

Eighty-four percent of the methyl chloroform is emitted directly to the atmosphere, 5 percent is discharged to municipal sewers and 8 percent is landfilled. Two percent is destroyed during the incineration of still bottoms and 1 percent is destroyed during carbon regeneration. The uncertainties for the environmental releases or destruction are calculated using the same factors as those for conveyorized vapor degreasers. The overall uncertainties are: +47 and -46 percent for releases to air; ±35 percent for releases to water; +52 and -47 percent for releases to land; +34 and -32 percent for the quantity incinerated and ±69 percent for the quantity destroyed during regeneration.

### 3.1.7 Multimedia Environmental Losses

Figure 3.1-12 shows the sum of the multimedia environmental losses from cold cleaning and vapor degreasing.

The overall uncertainty for air emissions for metal cleaning was calculated as follows:

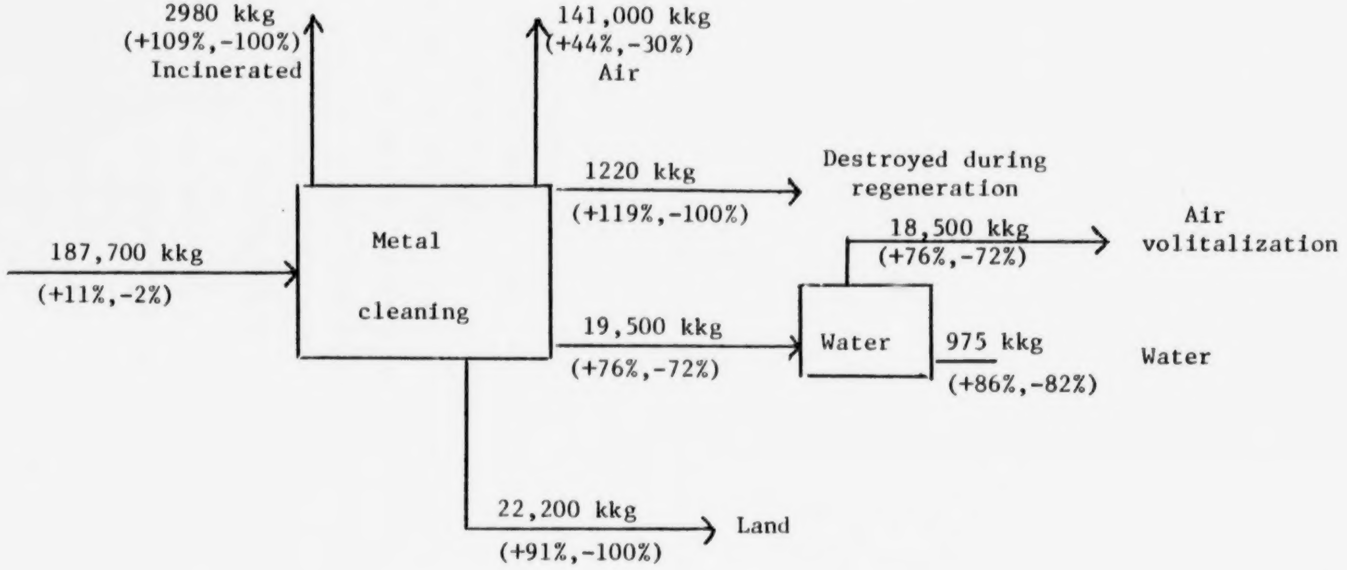

2980 kkg
(+109%,-100%)
Incinerated
141,000 kkg
(+44%,-30%)
Air
187,700 kkg
(+11%,-2%)
Metal
cleaning
1220 kkg
(+119%,-100%)
Destroyed during
regeneration
19,500 kkg
(+76%,-72%)
Water
18,500 kkg
(+76%,-72%)
Air
volitalization
975 kkg
(+86%,-82%)
Water
22,200 kkg
(+91%,-100%)
Land

Figure 3.1-12 Overall Multimedia Environmental Losses for Methyl Chloroform from Metal Cleaning

Upper Bound: subtract the lower limit of all other environmental losses from the upper limit of the total quantity of methyl chloroform used in metal cleaning.

(Total) 187,700 kkg (±11%) = 208,300 kkg
(Regeneration) 1,220 kkg (-100%) = (0)
(Landfilled) 22,200 kkg (-100%) = (0)
(Water) 19,500 kkg (-72%) = (5,500)
(Incinerated) 2,980 kkg (-100%) = (0)
202,800 kkg

$$\text{Upper Bound} = \frac{202{,}800\ \text{kkg}}{141{,}300\ \text{kkg}} \quad 1.44 \quad \text{or} \ +44\%$$

Lower Bound: subtract the upper limit of all other environmental losses from the lower limit of the total methyl chloroform used in metal cleaning.

(Total) 187,700 kkg (-2%) = 183,900 kkg
(Regeneration) 1,220 kkg (+119%) = (2,700)
(Landfilled) 22,200 kkg (+91%) = (42,400)
(Water) 19,500 kkg (+76%) = (34,300)
(Incinerated) 2,980 kkg (+109%) = (6,200)
98,300 kkg

$$\text{Lower Bound} = 1 - \frac{98{,}300\ \text{kkg}}{141{,}300\ \text{kkg}} = 0.30 \ \text{or} \ -30\%$$

The total quantity of air emissions from metal cleaning is 160,000 kkg. This figure includes 18,500 kkg of methyl chloroform (95 percent of 19,500 kkg) which volatilizes readily from waste water.

## 3.2 AEROSOL PRODUCTS

### 3.2.1 Quantification of Methyl Chloroform Used in Aerosol Products

Methyl chloroform is used as a solvent and a vapor depressant agent in many aerosol products. The quantity of methyl chloroform consumed in this category is not reported annually. It is estimated that about 18,000 kkg of this chemical was used in 1976 in the aerosol manufacturing industry (SRI, 1978; Chemical Marketing Reporter, 1977). Stanford Research Institute estimated that a 5 percent increase per year over 1976 could be expected for the consumption of methyl chloroform due to the ban of chlorofluorocarbon-based aerosol products from the consumer market (SRI, 1978). This would amount to a more than 10 percent increase in 1978 over 1976 consumption for aerosol uses. In that case, the total consumption of methyl chloroform in 1978 can be estimated by multiplying the quantity consumed in 1976 by the rate of increase.

| Methyl Chloroform Consumed in 1976 | x | Rate of Increase | = | Total Consumption of Methyl Chloroform in 1978 |
|---|---|---|---|---|
| (18,000 kkg) | | $(1.05)^2$ | = | 20,000 kkg |

The uncertainty of this figure is ±20% due to the uncertainty in the trend of aerosol consumption and the uncertainty of the total quantity consumed.

### 3.2.2 Use of Methyl Chloroform in Aerosol Products

Of the total quantity of methyl chloroform used in aerosol manufacture, 5,000 kkg is estimated to be consumed in the production of household products, automotive products, and coatings and finishes registered under the regulation of the Consumer Product Safety Commission (CPSC) (Battelle, 1979). The remaining 15,000 kkg is assumed to be consumed in the use of aerosols for personal care products (which are registered with the Food and Drug Administration (FDA)) and pesticide products (under the jurisdiction of the U.S. Environmental Protection Agency (EPA)). Information on the breakdown of different types of personal care products was not available in the literature. Because the use and formulation of these aerosol products are all similar, we can assume that the emission of methyl chloroform from aerosols is not affected by the lack of information on personal care products. Appendix D lists the registered pesticide products containing methyl chloroform (EPA Pesticide Files).

The following sections describe each methyl chloroform aerosol manufacturing process and the use of these aerosol products. Figure 3.2-1 shows a flow diagram of the use of methyl chloroform for aerosol products.

### 3.2.3 Use and Emissions of Methyl Chloroform in Household Aerosol Products

Methyl chloroform has been identified as a solvent used in many household aerosol products. JRB estimates that 60 percent of the total methyl chloroform consumed for products under the jurisdiction of CPSC is used in formulation of household products. This estimate is based solely on a 1975 estimate of the number of aerosol products used in household products as compared to the number used in coatings and finishing and automotive products. (Kirk-Othmer, 1971).

Based on this estimate, the quantity of methyl chloroform used in this category is calculated using the following equation.

| Total Methyl Chloroform Used in CPSC Registered Products | Percent Used in Household Products | = | Total Methyl Chloroform in Household Products |
|---|---|---|---|
| (5,000 kkg) | (0.6) | = | 3,000 kkg |

The uncertainty for the percent methyl chloroform used in household products is ±30%. Accounting for an uncertainty of ±20% for total methyl chloroform used in aerosol products, the overall uncertainty estimate is ±36%.

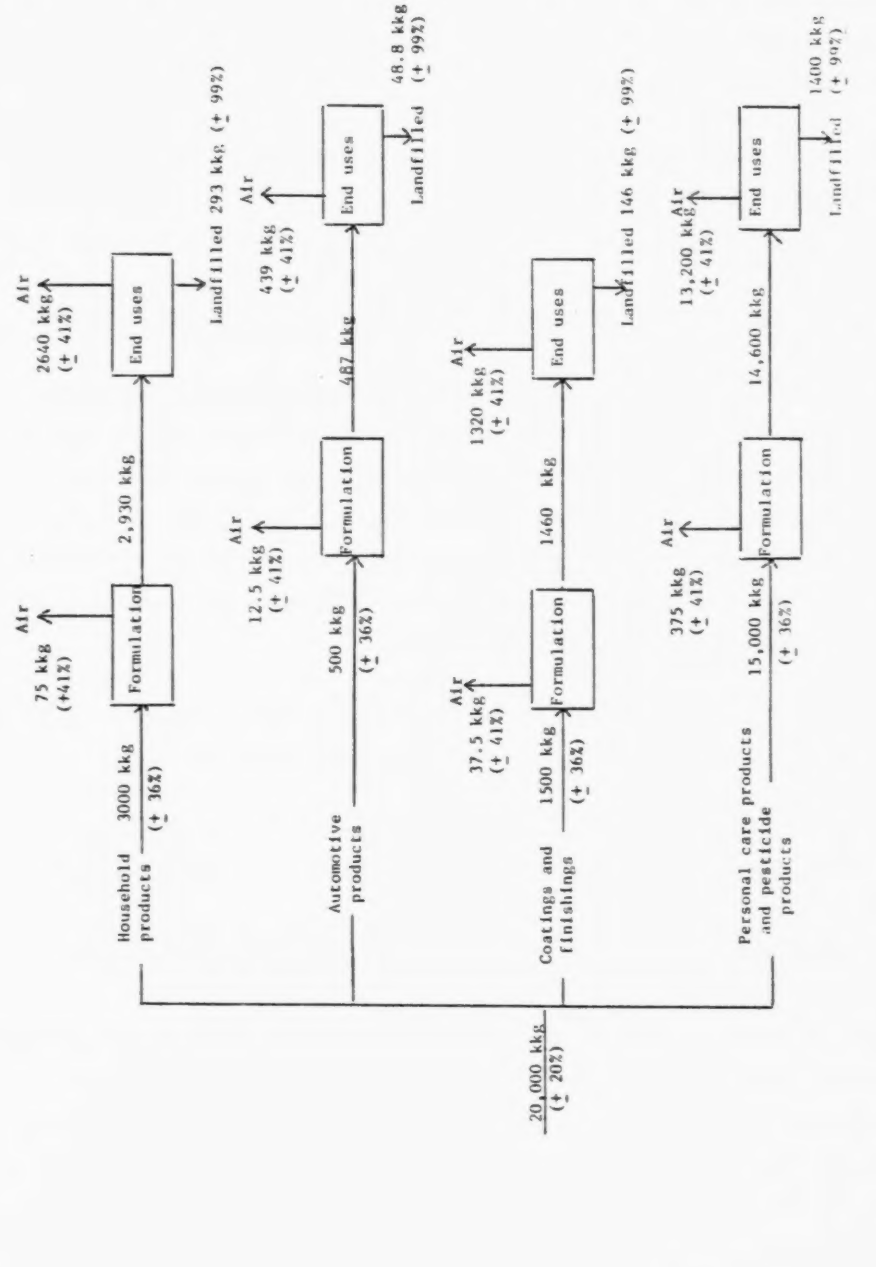

20,000 kkg
(± 20%)
Household products
3000 kkg
(± 36%)
Formulation
Air
75 kkg
(+41%)
2,930 kkg
End uses
Air
2640 kkg
(± 41%)
Landfilled 293 kkg (± 99%)
Automotive products
500 kkg
(± 36%)
Formulation
Air
12.5 kkg
(± 41%)
487 kkg
End uses
Air
439 kkg
(± 41%)
Landfilled
48.8 kkg
(± 99%)
Coatings and finishings
1500 kkg
(± 36%)
Formulation
Air
37.5 kkg
(± 41%)
1460 kkg
End uses
Air
1320 kkg
(± 41%)
Landfilled 146 kkg (± 99%)
Personal care products and pesticide products
15,000 kkg
(± 36%)
Formulation
Air
375 kkg
(± 41%)
14,600 kkg
End uses
Air
13,200 kkg
(± 41%)
Landfilled
1400 kkg
(± 99%)

Figure 3.2-1 Flow Diagram and Multimedia Environmental Losses of Methyl Chloroform from Aerosols

Methyl chloroform has been identified in the following household products (Battelle, 1979):

- -Adhesives
- -Dusting aid
- -Anti-static spray
- -Leather and suede products
  - *shoe polish formulation
  - *suede cleaner and conditioner
- -Spot remover
- -Fabric protector/water repellant
- -Metal cleaner/protective polish
- -Exhaust fan and hood cleaner
- -Mattress refresher
- -Teflon renewal
- -Miscellaneous

The chemical ingredient list of each product is shown in Appendix D.

### 3.2.3.1 Emissions to the Environment Due to the Formulation of Household Products

There is little information on the emission of methyl chloroform in the production of household aerosols. According to Johnson, it is estimated that the loss to the air during the formulation phase of aerosols can be as much as 2 to 3 percent of the consumption quantity (Johnson, 1979; Anthony, 1979). We feel that this percentage represents a good estimate of the emissions based on available information concerning the method used to fill aerosol cans. Thus, the total emission of methyl chloroform to the air during the production phase of household aerosols can be calculated as follows:

| Quantity of Methyl Chloroform in Household Products | Percent Lost During Formulation | = | Quantity of Methyl Chloroform Lost During Formulation |
|---|---|---|---|
| (3,000 kkg) | (0.025) | = | 75.0 kkg |

Emissions to land and water from production are estimated to be negligible due to the particular physical properties of methyl chloroform. Because this chemical is only slightly soluble in water (0.44g/100 ml @ 20° C) and is readily evaporated, we assume that all annual environmental emissions of methyl chloroform are to the air.

The uncertainty estimate for releases from formulation of household products is ±20%. The overall uncertainty is ±41% to account for possible deviations in the total quantity of methyl chloroform used in aerosols and the percent used in household products.

The quantity of methyl chloroform in aerosol products is estimated to be the difference between total methyl chloroform used in this cateogry and releases during formulation.

| Quantity of Methyl Chloroform for Household Products | | Quantity Released to Air During Formulation | = | Quantity Present in Household Aerosol Products |
|---|---|---|---|---|
| (3000 kkg) | - | (75 kkg) | = | 2,930 kkg |

### 3.2.3.2 Emissions to the Environment Due to Use of Household Aerosol Products

Based on typical consumer usage of aerosols, we assume that 90 percent of the contents of an aerosol package is used up and the remaining 10 percent remains in the package which will end up in municipal landfills.

The following expression is used to calculate the amount of methyl chloroform emitted to the air from the consumer use of aerosols:

| Quantity of Methyl Chloroform in Household Products | Percent Emitted to Air | = | Quantity Emitted to Air |
|---|---|---|---|
| (2930 kkg) | (0.9) | = | 2,640 kkg |

The overall uncertainty of this estimate is ±41%. This accounts for uncertainties related to total methyl chloroform used for aerosol products, the percent used for household products and the percent emitted to air, which has an uncertainty estimate of ±5%.

The remaining 10 percent is retained in aerosol containers and is disposed in landfills as residue.

| Quantity of Methyl Chloroform in Household Products | Percent Retained in Containers | = | Amount Disposed to Landfills |
|---|---|---|---|
| (2930 kkg) | (0.1) | = | 293 kkg |

With an uncertainty of ±90% for the percent of methyl chloroform retained in aerosol cans, the overall uncertainty for the quantity released to land is ±99%.

### 3.2.4 Use and Emissions of Methyl Chloroform in Automotive Products

Methyl chloroform is used in automotive products for metal degreasing and carburator cleaning. Based upon the number of automotive aerosol products sold in 1975 relative to household products and coatings and furnishing, JRB estimates that 10 percent of the methyl chloroform in CPSC registered products was used in automotive products (Kirk-Othmer, 1971). Based upon this estimate, the quantity of methyl chloroform in aerosol automotive products is estimated as follows:

| Total Methyl Chloroform in Methyl CPSC Registered Products | Percent which are Automotive Products | = | Quantity of Chloroform in Automotive Aerosol Products |
|---|---|---|---|
| (5000 kkg) | (0.1) | = | 500 kkg |

This estimate is considered accurate to ±36% considering the uncertainties related to total methyl chloroform used in aerosol products (±20%) and the uncertainty for the percent used in automotive products (±30%).

Methyl chloroform has been listed as an ingredient in the following automotive products (Battelle, 1979):

-Engine degreaser and cleaner
-Brake cleaner
-Belt dressings
-Lubricants.

A list of chemical ingredient formulations of the automotive aerosol products is itemized in the Appendix D.

### 3.2.4.1 Emissions to the Air During the Formulation Phase

Assumptions similar to those established in Section 3.2.3.1 also apply here. We estimate that from 2 percent to 3 percent of the total consumption of methyl chloroform for aerosol uses is emitted to the air during the production phase. The emission to the air during the production of automotive aerosol products can then be calculated by multiplying the quantity of methyl chloroform available for the production of automotive products by the emission factor of 2.5 percent:

| Quantity of Methyl Chloroform in Automotive Products | Percent Released During Formulation | = | Quantity Released During Formulation |
|---|---|---|---|
| (500 kkg) | (0.025) | = | 12.5 kkg |

The uncertainty of this estimate is ±41%. This range accounts for uncertainties related to quantities of methyl chloroform in aerosol products, the percent used in automotive products and the quantity released during formulation.

### 3.2.4.2 Emissions to the Environment Due to the Use of Automotive Products

The use of automotive aerosol products is not unlike that of household products. Thus, we can assume that 90 percent of the contents of an aerosol package is released by spraying and the remaining 10 percent is landfilled as residue in used containers.

The emission to air from the use of automotive products is estimated as follows:

| Quantity Methyl Chloroform in Automotive Products | - | Releases to Air During Formulation | x | Percent Emitted to Air | = | Quantity Emitted to Air |
|---|---|---|---|---|---|---|
| (500 kkg | - | 12.5 kkg) | x | (0.9) | = | 439 kkg |

The quantity landfilled is estimated as follows:

| Quantity of Methyl Chloroform in Automotive Products | - | Releases to Air During Formulation | x | Percent Landfilled | = | Quantity Landfilled |
|---|---|---|---|---|---|---|
| (500 kkg | - | 12.5 kkg) | x | (0.1) | = | 48.8 kkg |

The overall uncertainty estimates for the quantity of methyl chloroform emitted to air and landfilled are ±41% and ±99% respectively. These ranges account for uncertainties related to the total quantity of methyl chloroform used in aerosols, the percent used in automotive products and the percent released to air or landfilled.

### 3.2.5 Use and Emissions of Methyl Chloroform in Coatings and Finishes

Methyl chloroform has also found use in the production of lacquer stains, fixative and protective coatings, racing bottom treatment reagent, and polyurethane coatings. The list of chemical ingredients of these products is shown in the Appendix D.

We assume that the remaining 30 percent of the total consumption of methyl chloroform for the production of aerosols registered with the CPSC is consumed in the coating and finishing products business. Again, this estimate is based solely on the number of aerosol containers sold in 1975 in this product category, relative to household and automotive products.

The consumption of methyl chloroform in coating and finishing can be calculated from the following equation:

| Total Methyl Chloroform in CPSC Registered Products | Percent Used in Coatings and Finishes | = | Quantity Used in Coatings and Finishes |
|---|---|---|---|
| (5000 kkg) | (0.3) | = | 1500 kkg |

The uncertainty of this estimate is ±36%, based on the uncertainty of the total methyl chloroform used in aerosol products (±20%) and the uncertainty of the quantity used in coatings and finishes (±30%).

### 3.2.5.1 Emissions During the Production Phase

It is estimated that air emissions account for all methyl chloroform releases during the production phase. The emission factor is assumed to be 2.5 percent (see Section 3.2.3.1) with an uncertainty value of ±20%. Based on these conditions, the atmospheric emission of methyl chloroform from the production of coating and finishing products can be estimated as follows:

| Methyl Chloroform in Coating and Finishing Products | Percent Emitted to Air During Formulation | = | Quantity Emitted to Air |
|---|---|---|---|
| (1500 kkg) | (0.025) | = | 37.5 kkg |

The overall uncertainty for this estimate is ±41%.

### 3.2.5.2 Emissions from the Uses of Coating and Finishes

The emission to the air from the use of coating and finishing products are again estimated to be 90 percent of the total emissions.

| Quantity of Methyl Chloroform in Coating and and Finishing Products | - | Quantity Emitted to Air During Formulation | x | Percent Emitted to Air from Use | = | Quantity Emitted to Air |
|---|---|---|---|---|---|---|
| (1500 kkg | - | 37.5 kkg) | x | (0.9) | = | 1320 kkg |

The remaining 10 percent is landfilled as residual in discarded containers.

| Quantity of Methyl Chloroform in Coating and Finishing Products | - | Quantity Emitted to Air During Formulation | x | Percent Landfilled | = | Quantity Landfilled |
|---|---|---|---|---|---|---|
| (1500 kkg | - | 37.5 kkg) | x | (0.1) | = | 146 kkg |

The uncertainty of the estimates for the quantity released to air and landfilled are ±41% and ±99% respectively.

### 3.2.6 Use and Emissions of Methyl Chloroform in Personal Care Products and Pesticides Products

As mentioned in Section 3.2.1, it is estimated that 15,000 kkg of methyl chloroform was consumed in the process of manufacturing personal care and pesticide products. The use of methyl chloroform in personal care products is regulated by the Food and Drug Administration (FDA). Pesticide products are under the jurisdiction of the Environmental Protection Agency (EPA). There is little information on the use of methyl chloroform for the production of these aerosols. We assume that it is used as a solvent and as a vapor pressure depressing agent. A list of methyl chloroform containing pesticide aerosol products is shown in Appendix D.

#### 3.2.6.1 Emission to the Air During the Production Phase

Again, since the manufacturing processes are similar to those of the household product industry, we assume from 2 percent to 3 percent methyl chloroform is released to the air during the production of these aerosol products. Therefore, we estimate that the emission factor is 2.5 percent of the total consumption for the production process with a deviation of ±20%. The emission to the air from the production of the personal care and pesticide aerosol products are then estimated as follows:

| | | | |
|---|---|---|---|
| Total Methyl Chloroform in Personal Care and Pesticide Products | Percent Emitted During Formulation | = | Quantity Emitted During Formulation |
| (15,000 kkg) | (0.025) | = | 375 kkg |

The overall uncertainty of this estimate is ±41% to account for uncertainties related to total methyl chloroform used in aerosols (±20%), quantity used in personal care and pesticide products (±30%) and the percent emitted to air during formulation (±20%).

### 3.2.6.2 Emissions to the Environment Due to the Use of Personal Care and Pesticide Products

It is estimated that 90 percent of the contents in an aerosol package is consumed and 10 percent remains intact in the package and is disposed of in landfills (see Section 3.2.3.2). These are only estimates and should be verified by later studies.

The total release of methyl chloroform to the air due to the use of personal care and pesticide products can then be calculated from the following equation:

| | | | | | | |
|---|---|---|---|---|---|---|
| Methyl Chloroform in Personal Care and Pesticide Products | - | Quantity Lost During Formulation | x | Percent Emitted to Air | = | Quantity Emitted to Air |
| (15,000 kkg | - | 375 kkg) | x | (0.9) | = | 13,200 kkg |

The amount of methyl chloroform that is considered to be disposed in landfills can be estimated as follows:

| | | | | |
|---|---|---|---|---|
| (Total Quantity) | - | (Air Emissions) | = | Quantity landfilled |
| (14,600 kkg) | - | (13,200 kkg) | = | 1,400 kkg |

The uncertainties of these figures are ±41% for the quantity emitted to air and ±99% for the quantity landfilled.

### 3.2.7 Multimedia Environmental Losses

Figure 3.2-2 summarizes the environmental releases of methyl chloroform from the production and use of aerosol products.

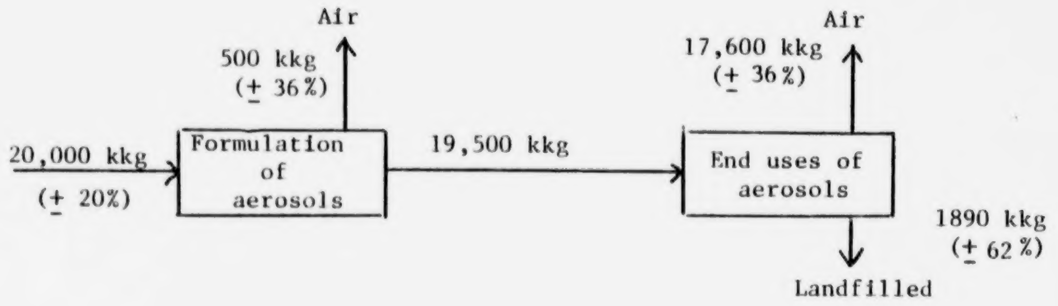

20,000 kkg
(± 20%)
Formulation of aerosols
500 kkg
(± 36%)
Air
19,500 kkg
End uses of aerosols
17,600 kkg
(± 36%)
Air
1890 kkg
(± 62%)
Landfilled

Figure 3.2-2 Multimedia Environmental Losses of Methyl Chloroform from the Production and Use of Aerosols*

* Numbers may not add due to rounding

## 3.3 ADHESIVES

Approximately 20 percent of all adhesives produced annually are solvent based (Effluent Guidelines, 1979). Solvent based adhesives have an advantage over water based types because they are generally more tacky and provide high early bond strength. Chlorinated solvents are used in specific applications to increase the solvency of an adhesive and where non-flammable solvents are required. They are also used selectively in making resin emulsions or elastomers for water based adhesives.

### 3.3.1 Quantification of Methyl Chloroform Used in Adhesives

Although raw materials used in the production of adhesives have been quantified in the 1977 Census of Manufacturers (Adhesives Age, 1979), solvents were not included in this inventory. A rough estimate of the total chlorinated solvents used in the adhesives industry has been made by researchers at Skeist Laboratories. It was estimated that 27,000 kkg of chlorinated solvents (±20%) were used in adhesives, and methyl chloroform was by far the major chlorinated solvent used (Miron, J., Skeist Labs, 1979). Chemical Marketing Reporter estimated that 19,800 kkg of methyl chloroform are used in the production of adhesives (Chemical Marketing Reporter, 1977). This estimate is 73 percent of the estimate made by Skeist Labs for total chlorinated solvents and thus seems reasonable when one considers that methyl chloroform is the major chlorinated solvent used. For purposes of the materials balance calculations, 19,800 kkg of methyl chloroform (±20%) will be used.

Contacts with the adhesives industry, however suggest that the status of methyl chloroform as a solvent for adhesives is changing. Hercules, which sells resins for adhesives, indicated that many of their clients are phasing out solvent based adhesives and substituting "hot melts" and water based types (Hercules, 1979). Contacts at National Starch, UPACO and Mobay Chemicals also indicated that solvent based adhesives were being phased out, wherever possible. These changes are a result of existing or potential regulations imposed by State Implementation

Plans, the Clean Air Act Amendments, and OSHA requirements (Reich, J., 1979; Sweeny, T., 1979; and Witzman, C., 1979) (see Appendix B). Industry contacts did not distinguish between currently exempt and non-exempt solvents when discussing their programs for phasing out the use of solvents, since manufacturers felt that currently exempt solvents would also be regulated.

### 3.3.2 Use of Methyl Chloroform in the Adhesives Industry

Table 3.3-1 lists the 15 product subcategories for adhesives, 1977 production data for each subcategory, and the percentage of plants using methyl chloroform (Effluent Guidelines, 1979).

Since adhesive plants often produce many formulations within several subcategories, plants using methyl chloroform for production of adhesives in one subcategory may be "double counted" in another subcategory. For example, many plants producing solvent based resin adhesives also produce solvent based elastomer adhesives. Although methyl chloroform may only be used in one subcategory, it would appear, in Table 3.3-1, in the other as well. The geographic distribution of plants using methyl chloroform was not available for this study. However, Figure 3.3-1 shows that the adhesives industries in general are concentrated in the northeast, and to a lesser extent in the Great Lakes area and Texas. The results of the effluent guidelines survey, summarized in Table 3.3.1, indicated the following with respect to methyl chloroform:

- Methyl chloroform is used in the production of water based adhesives as well as solvent based types.
- Further analysis of the survey results indicated that 50 plants within subcategories 1-7 used methyl chloroform (a total of 70 plants, shown for subcategories in Table 3.3-1 , indicates that many plants are making adhesives in more than one subcategory and are therefore "double counted").
- Among the plants producing water based adhesives, methyl chloroform is most widely used in production of synthetic resin-based adhesives.

## Table 3.3-1 Adhesive Subcategories

| Subcategory | Number of Plants | Annual Production kkg | Number of Plants Using Methyl Chloroform | Percent of Plants Using Methyl Chloroform |
|---|---|---|---|---|
| Solution of protein material in water | 87 | 90,350 | 0 | 0 |
| Solution of carbohydrates in water | 110 | 129,400 | 8 | 7% |
| Solution of inorganic materials in water | 31 | 518,000 | 1 | 3% |
| Dispersion of natural elastomer in water | 74 | 15,000 | 2 | 3% |
| Solutions or dispersions of other natural organics in water | 46 | 23,000 | 4 | 9% |
| Solutions or dispersions of synthetic elastomers in water | 113 | 532,000 | 7 | 6% |
| Solutions, emulsions, dispersions of synthetic resins in water | 208 | 606,600 | 48 | 23% |
| Solutions of natural organic compound in water | 54 | 44,500 | 5 | 9% |
| Solutions, dispersions of natural elastomer in solvent | 48 | 29,500<br>$210 \times 10^6$L | 8 | 17% |
| Solutions of synthetic resin in solvent | 139 | 91,300 | 21 | 15% |
| Solution of synthetic elastomer in solvent | 116 | 164,000 | 39 | 34% |
| 100% sythetic or natural resin, "hot melt" products | 79 | 180,100 | 0 | 0 |
| Chemically reactive | 73 | 52,700 | 1 | 1% |
| Dry blends | 45 | 78,500 | 0 | 0 |
| Others | 14 | 33,200 | 6 | 43% |

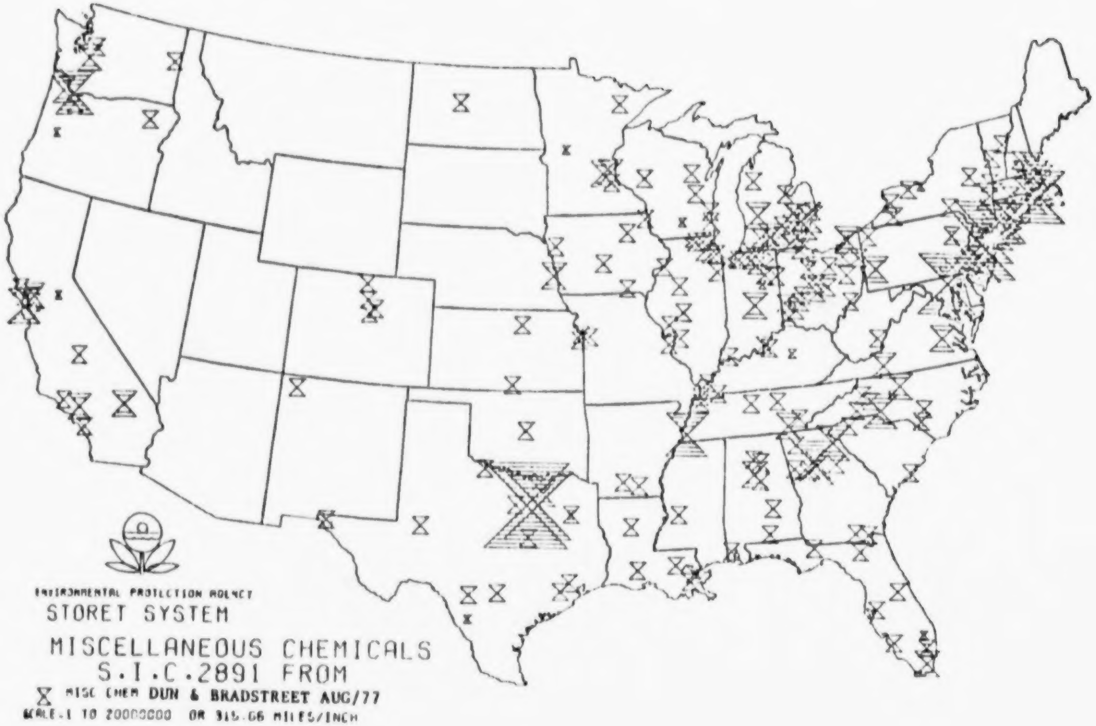

ENVIRONMENTAL PROTECTION AGENCY
STORET SYSTEM
MISCELLANEOUS CHEMICALS
S.I.C.2891 FROM
X MISC CHEM DUN & BRADSTREET AUG/77
SCALE-1 TO 20000000 OR 315.66 MILES/INCH

Figure 3.3-1 Georgraphic Distribution of Adhesive Industries

- Forty-nine producers of solvent based adhesives use methyl chloroform. Only the solvent toluene was used by more plants producing solvent based adhesives. The chlorinated solvents methylene chloride and trichloroethylene were used much less frequently; 34 percent fewer plant-subcategories reported using methylene chloride and 71 percent fewer used trichloroethylene (Effluent Guidelines, 1979).
- Among producers of solvent based adhesives, methyl chloroform was used most widely among producers of synthetic elastomers and synthetic resins in solvent.
- The survey further indicated that although half the plants using methyl chloroform produced water based adhesives, these plants, as expected, use less solvent.

Based on calculations presented in Sections 3.3.3 and 3.3.4, JRB estimated that approximately 20 percent of the methy chloroform used in the adhesives industry is used for production of solvent based adhesives. This estimate seemed "reasonable" to one industrial contact with whom several of JRB's assumptions were reviewed (industrial contact, 1979).

### 3.3.3 Use and Emissions of Methyl Chloroform in Solvent Based Adhesives

Solvents have three uses in the production of solvent based adhesives:

#### 1) Dissolution of Natural and Synthetic Rubber and Synthetic Resins

Solvent based adhesives are prepared by dissolving the milled elastomer or resin in solvent within enclosed churns or mixers. The volume of methyl chloroform can vary from 5 percent where other solvents are also used to 90 percent where methyl chloroform is the only solvent (Hall, J., 1979). Solvent losses during formulation are low since dissolution is carriedout in enclosed vessels (Hall, J., 1979; Wilholdt Cement, 1979). Vapor recovery systems have been included in many solvent based adhesive operations to recover solvent losses (Effluent Guidelines, 1979).

### 2) Solution Polymerization

A monomer or monomer mixture is dissolved in solvents and polymerization is effected at elevated temperatures in the presence of an initiator. Solvents used in this process must be inert to free radicals (Skeist, 1977) and consequently chlorinated solvents would not be used.

### 3) Cleaning of Vessels or Reactor

Chlorinated solvents are used in cleaning up spills in vessels and reactors. It is likely that methyl chloroform would be used more widely among plants using this solvent in their formulations. Spent solvent is often given to outside contractors (Effluent Guidelines, 1979).

Figure 3.3-2 shows estimated losses of methyl chloroform from solvent based adhesives. These estimates were based largely on engineering judgements although assumptions were verified with industrial contacts where possible. Although several industrial contacts were made, JRB could not generalize for the industry as a whole; typically an adhesive plant produces adhesives in several subcategories and changes formulations frequently. A more accurate estimate of methyl chloroform losses would require a survey of the industry.

### 3.3.3.1 Vessel Cleaning

This section estimates the amount of methyl chloroform used to clean vessels and quantifies environmental releases through various media. Based on the Effluent Guidelines profile of the industry, about one-third of all plants surveyed use solvent cleaning, although many use caustic wash and dry wash as well. (Effluent Guidelines, 1979) About 50 percent of the plants produced some solvent based adhesives (Effluent Guidelines, 1979).

Therefore:

| | | | |
|---|---|---|---|
| Number of Plants Surveyed | Percent Using Solvent Cleaning | = | No. of Plants Using Solvent Cleaning |
| (322) | (0.33) | = | 106 plants |
| Number of Plants Plants Surveyed | Percent Producing Solvent Based Adhesives | = | No. of Plants Producing Solvent Based Adhesives |
| (322) | (0.5) | | = 161 plants |

If we assume that plants using solvent for cleaning are also those plants which produce solvent based adhesives, then the percentage using solvent for cleaning is:

$$\frac{106 \text{ plants}}{161 \text{ plants}} = 65\% \text{ using some solvent cleaning}$$

Vessels used for adhesives formulation can range in size from 400 liters to 18,750 liters (Effluent Guidelines, 1979); an average vessel was assumed to be 7,500 liters. JRB also assumed that an average wash would require a volume of solvent 1/10 the vessel size (1 kkg solvent) and that methyl chloroform is used in 1/3 of the solvent washings. Other solvents may include methylene chloroide and toluene. Changes in formulation may be very frequent in some industries but cleaning frequency could be reduced by switching to a similar formulation. It was assumed that a typical plant would operate about 5 vessels and that cleaning would be required biweekly. Then, the total quantity of methyl chloroform used for solvent vessel cleaning is estimated using the following equation:

| Quantity of Methyl Chloroform Per Vessel | Number of Vessels Per Plant | Percent Using Solvent Cleaning | Number of Plants Using Methyl Chloroform | Percent of Solvent which is Methyl Chloroform |
|---|---|---|---|---|

| Number of Cleaning /Year | = | Total Methyl Chloroform used for Cleaning |
|---|---|---|

$$1 \text{ kkg/vessel} \times 5 \ \frac{\text{vessels}}{\text{plant}} \times 0.65 \times 50 \text{ plants} \times 0.3 \times 26/\text{yr} = \underline{1270 \text{ kkg}}$$

If another 10 percent is used for cleanup of spills, then:

1270 kkg (0.1) = 127 kkg solvent for spills

The estimate of 1400 kkg methyl chloroform used for vessel cleaning is considered accurate to +30% and -50% to account for uncertainties related to solvent cleaning practices, and "typical" plant conditions which effect the quantity of solvent needed.

Environmental Releases from Vessel Cleaning

JRB assumes that about 15 percent of the solvent is emitted to air during cleaning of vessels or spills. No information is available on this topic and this estimate is based on engineering judgment. Therefore:

| Total Solvent Used for Cleaning | Percent Emitted | = | Total Lost to Air from Cleaning |
|---|---|---|---|
| (1400 kkg) | (0.15) | = | 210 kkg |

The Effluent Guidelines Survey indicated that many plants using solvents for cleaning contract their waste solvent for reclamation. However, no quantitative estimates were made for solvent reclamation. JRB assumed that 65 percent of the plants contract their waste solvent for solvent recovery, which is assumed to operate at 95 percent efficiency (Effluent Guidelines, 1979; EPA, 1979e). This reclaimed solvent is assumed to be sold for use outside the industry. Larger plants may be equipped with their own solvent reclamation equipment which would probably operate at slightly lower efficiency. It is assumed that

15 percent of the plants reclaim the solvent in-house at 90 percent efficiency and that this solvent is reused. It is probable that solvent recovery services incinerate the remaining still bottoms (5 percent) at 95 percent efficiency (±4%) and that still bottoms resulting from in-house reclamation are landfilled. Finally, the remaining 35 percent of the waste solvent is assumed to be discharged. The following series of calculations estimates releases of waste solvent from reclamation and disposal:

| Total Solvent Used for Cleaning - Atmospheric Losses from Cleaning | Percent of Plants Using Outside Solvent Reclamation Services | Efficiency of Reclamation | = | Methyl Chloroform Reclaimed |
|---|---|---|---|---|
| (1400 kkg - 210 kkg) | (0.65) | (0.95) | = | 735 kkg |

This reclaimed solvent is sold to users outside the adhesive industry.

| Total Solvent Used for Cleaning - Atmospheric Losses from Cleaning | Percent of Plants Using Outside Recovery Services | Percent Incinerated | = | Quantity of Methyl Chloroform Incinerated |
|---|---|---|---|---|
| (1400 kkg - 210 kkg) | (0.65) | (0.05) | = | 45.5 kkg |

| Quantity of Methyl Chloroform Incinerated | 1-Incineration Efficiency | = | Air Emisions of Methyl Chloroform from Incineration |
|---|---|---|---|
| (45.5 kkg) | (1- 0.95) | = | 2.28 kkg |

| Quantity of Methyl Chloroform Incinerated | Incineration Efficiency | = | Quantity of Methyl Chloroform Destroyed |
|---|---|---|---|
| (45.5 kkg) | (0.95) | = | 43.2 kkg |

| Total Solvent Used for Cleaning | - | Atmospheric Losses from Cleaning | Percent Recovered In-house | Percent Efficiency | = | Methyl Chloroform Reclaimed In-house |
|---|---|---|---|---|---|---|
| (1400 kkg | - | 210 kkg) | (0.15) | (0.9) | = | 161 kkg |

| Total Solvent Used for Cleaning | - | Atmospheric Losses from Cleaning | Percent Recovered In-house | Percent Landfilled | = | Quantity Methyl Chloroform Landfilled |
|---|---|---|---|---|---|---|
| (1400 kkg | - | 210 kkg) | (0.15) | (0.10) | = | 17.9 kkg |

| Total Solvent Used for Cleaning | - | Atmospheric Losses From Cleaning | Percent Discharged | = | Quantity Discharged |
|---|---|---|---|---|---|
| (1400 kkg | - | 210 kkg) | (0.20) | = | 238 kkg |

It is assumed that 95 percent of this quantity or 226 kkg are volatilized before stream discharge and the remaining 12 kkg remain in water.

JRB's uncertainty estimates for the percent releases to various media are tabulated below. The individual uncertainties account for uncertainties related to solvent cleaning practices, the extent to which reclamation is practiced and waste solvent disposal practices. Table 3.3-2 also shows overall uncertainties which account for an uncertainty of +30% and -50% for total methyl chloroform used in vessel cleaning.

Table 3.3-2 - Summary of Uncertainties for Environmental Releases from Vessel Cleaning

| Source | Quantity (kkg) | Percentage of Individual Uncertainty (%) | Percentage of Overall Uncertainty (%) |
|---|---|---|---|
| Solvent emitted to air | 210 | ±25 | +39/-56 |
| Solvent reclaimed by outside services | 565 | +10/-30 | +40/-64 |
| Still Bottoms Incinerated | 45.5 | +10/-30 | +40/-64 |
| Air Emissions Incinerator | 2.28 | ±80 | +89,-100 |
| Methyl Chloroform Destination (Incineration) | 43.2 | ±4 | +40,-64 |
| Solvent Reclaimed In-house | 161 | ±25 | +46/-61 |
| Still Bottoms Landfilled | 17.9 | ±25 | +46/-61 |
| Solvent Discharged | 238 | +30/-10 | +49/-57 |

### 3.3.3.2 Methyl Chloroform Losses from Solvent Based Cement Products

Several industry contacts indicated that rubber based cements, especially neoprenes, are the largest single user of methyl chloroform in the adhesive industry. However, no contacts would venture to estimate what percentage of methyl chloroform used in solvent based adhesives is used in rubber based cements.

Because we were unable to identify any large users of methyl chloroform for other subcategories of adhesives, it is assumed that rubber based cements (synthetic elastomers) used 85 percent of the methyl chloroform used in solvent based adhesives. Solvent based adhesives are typically 20 percent solids (Skeist, 1977; Effluent Guidelines, 1979) and approximately 10 percent of the solvent based cements contain methyl chloroform as compared to other solvents (based on contact with Wilholdt Glues only, 1979). Using 1977 production data for synthetic elastomers in solvent (including neoprene cements, SBR, NBR, Butyl and polyiso-butyl cements) we can estimate total methyl chloroform used in this subcategory. 1977 production is estimated at 164 x $10^3$ kkg for this subcategory. (Effluent Guidelines, 1979)

| Total Production of Synthetic Elastomers in Solvent | Percent Solvent in Solvent-based Cements | Percent Solvent Based Cements with Methyl Chloroform | = | Methyl Chloroform in Solvent Based Cements |
|---|---|---|---|---|
| (164 x $10^3$ kkg) | (0.1) | (0.8) | = | 13,100 kkg |

If this quantity represents 85 percent of all methyl chloroform used in solvent based adhesives, then total methyl chloroform in solvent based adhesives is estimated as follows:

$$\frac{\text{Methyl Chloroform in Rubber Cements}}{\text{Percent of Methyl Chloroform in Rubber Based Cements}} = \text{Total methyl chloroform in solvent based adhesives}$$

$$13{,}100 \text{ kkg}/0.85 = 15{,}400 \text{ kkg}$$

This estimate is considered accurate to ±15% to account for uncertainties related to the quantity of solvent in solvent based adhesives products.

Contacts with industry (Hall, J., 1979; Wilholdt Cement, 1979) indicated that very small amounts of solvent are lost in production, and may account for only 0.5 percent of the solvent. JRB considers this estimate to be accurate to +50% and -22%.

$$(15{,}400 \text{ kkg})\ (0.005) = 77.0 \text{ kkg lost in the process.}$$

Accounting for an uncertainty of ±15% for the total methyl chloroform in products, the overall uncertainty is +52% and -25%.

It was assumed that 95 percent of the methyl chloroform in end products is lost to the air and 5 percent is landfilled when used adhesives containers are disposed of.

These quantities are estimated using the following expression:

| | | | | | |
|---|---|---|---|---|---|
| Total Methyl Chloroform in Solvent Based Adhesives | - | Quantity Released During Production | Percent Released to Air | = | Quantity Emitted to Air from End Use of Products |
| (15,400 kkg | - | 77.0 kkg) | (0.95) | = | 14,600 kkg |

| | | | | | |
|---|---|---|---|---|---|
| Total Methyl Chloroform in Solvent Based Adhesives | - | Quantity Released During Production | Percent Released to Land | = | Quantity Emitted to Land from End Use of Products |
| (15,400 kkg | - | 77.0 kkg) | (0.05) | = | 766 kkg |

The quantity of methyl chloroform emitted to air from use of solvent based adhesives is accurate to ±5% and the quantity landfilled is accurate to ±75%.

Accounting for an uncertainty estimate of ±15% for the total methyl chloroform in solvent based adhesive products, the overall uncertainty is ±16% for releases to air and ±76% for releases to land.

Figure 3.3-2 indicates that 96 percent of the solvent used in solvent based adhesives is lost to the environment or destroyed and 4 percent is recycled. Solvent losses from end products account for 97 percent of the total solvent lost. Less than 1 percent of the solvent is emitted directly to the atmosphere from vessel cleaning or from product formulation. Another two percent is discharged to wastewater treatment and about 0.2 percent is landfilled. The remaining waste solvent, amounting to 0.2 percent, is destroyed by incineration.

Since most solvent losses are from product end use, several industries were contacted to determine the major end uses of their solvent based adhesives. It was learned that solvent based cements are used widely in construction related activities, and in consumer contact cements. They are also used in the automotive industry, the shoe and textile industries and in preparation of pressure sensitive tapes. (Miron, J., 1979; Witzman, C., 1979; Hall, J., 1979).

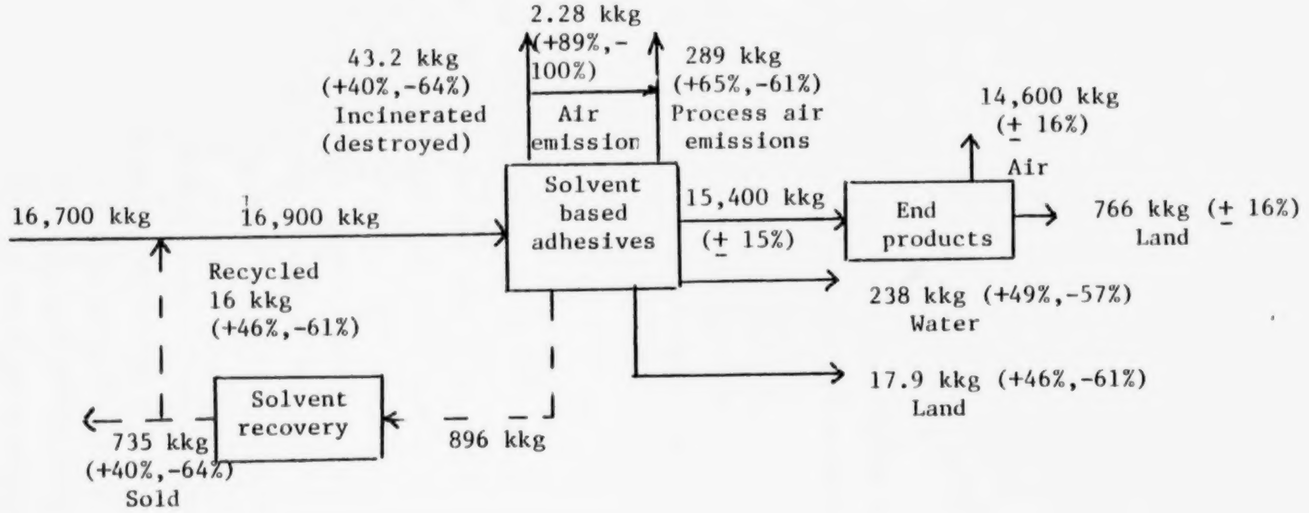

16,700 kkg
16,900 kkg
Recycled
16 kkg
(+46%,-61%)
735 kkg
(+40%,-64%)
Sold
Solvent
recovery
896 kkg
43.2 kkg
(+40%,-64%)
Incinerated
(destroyed)
2.28 kkg
(+89%,-
100%)
Air
emission
289 kkg
(+65%,-61%)
Process air
emissions
Solvent
based
adhesives
15,400 kkg
(± 15%)
End
products
14,600 kkg
(± 16%)
Air
766 kkg (± 16%)
Land
238 kkg (+49%,-57%)
Water
17.9 kkg (+46%,-61%)
Land

Figure 3.3-2 Multimedia Environmental Losses of Methyl Chloroform from Solvent Based Adhesives

No quantitative breakdown of losses from end uses could be obtained within the scope of the study.

### 3.3.4 Use and Emissions of Methyl Chloroform in Water Based Adhesives

Solvent losses from water based adhesives result from the use of solvents in emulsions and from cleaning vessels and reactors. Solvent washing of vessels and reactors is not common among plants formulating only water based adhesives. Furthermore, even in plants that produce both water based and solvent based adhesives, solvent cleaning is probably less frequent during formulation of water based adhesives. Most of the compounds used in formulation of water based adhesives are water soluble and might not require expensive chlorinated solvents for cleaning. In formulating emulsions, chlorinated solvents can be used to facilitate adhesion. As with solvent based adhesives, solvent use can be highly variable. Again, process losses are expected to be small because of the use of vapor recovery systems and enclosed mixers.

Figure 3.3-3 shows estimated losses of methyl chloroform from the formulation and use of water based adhesives.

#### 3.3.4.1 Vessel Cleaning

It was assumed that only 25 percent of plants making water based adhesives used solvent cleaning. All other assumptions were the same as those made for solvent based adhesives. Using these assumptions, the following estimates were made:

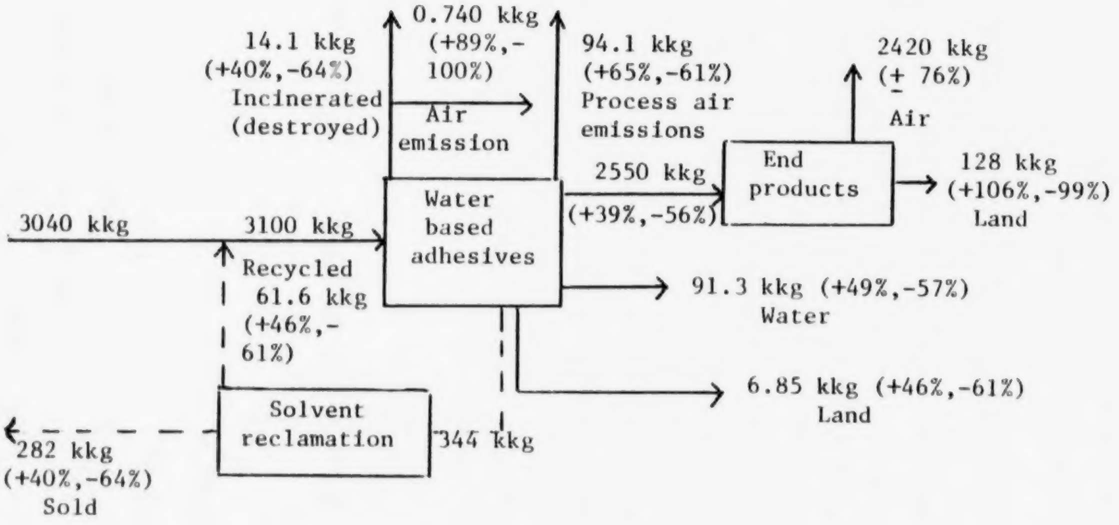

3040 kkg
3100 kkg
Recycled
61.6 kkg
(+46%,-
61%)
14.1 kkg
(+40%,-64%)
Incinerated
(destroyed)
0.740 kkg
(+89%,-
100%)
Air
emission
94.1 kkg
(+65%,-61%)
Process air
emissions
Water
based
adhesives
2550 kkg
(+39%,-56%)
End
products
2420 kkg
(± 76%)
Air
128 kkg
(+106%,-99%)
Land
91.3 kkg (+49%,-57%)
Water
6.85 kkg (+46%,-61%)
Land
Solvent
reclamation
344 kkg
282 kkg
(+40%,-64%)
Sold

Figure 3.3-3 Multimedia Environmental Losses of Methyl Chloroform from Water Based Adhesives

| Quantity of Solvent per Vessel for Cleaning | | Number of Vessels Per Plant | Percent of Plants which Use Solvent Cleaning | Number of Plants Using Methyl Chloroform | Percent Methyl Chloroform Used in Solvent | Number of Cleanings Per Year | | Total Methyl Chloroform Used for Vessel Cleaning |
|---|---|---|---|---|---|---|---|---|
| (1 kkg/vessel) | x | (5 $\frac{\text{vessels}}{\text{plant}}$) | (0.25) | (50 plants) | (0.3) | (26) | = | 488 kkg |

Assuming another 10 percent is used to clean up spills, the total quantity used for cleaning is then equal to the quantity used to clean vessels plus the quantity used to clean spills.

(488 kkg) + (48.8 kkg) = 537 kkg

This estimate for methyl chloroform used in vessel cleaning is not considered more accurate than +30% and -50%.

### Emissions from Cleaning Vessels from Water Based Adhesives

Using assumptions discussed in Section 3.3.3.1, for solvent based adhesives the following estimates are made.

| Total Solvent Used for Cleaning | Percent Emitted to Air | | Quanity Released |
|---|---|---|---|
| (537 kkg) | (0.15) | = | 80.6 kkg |

| Quantity of Solvent Used in Cleaning | | Quantity Emitted to Air | Percent Reclaimed by Outside Contractor | Efficiency of Solvent Recovery | | Quantity Reclaimed by Outside Contractor |
|---|---|---|---|---|---|---|
| (537 kkg | - | 80.6 kkg) | (0.65) | (0.95) | = | 282 kkg |

| | | | | | | |
|---|---|---|---|---|---|---|
| Quantity of Solvent Used in Cleaning | - | Quantity Emitted to Air | Percent Reclaimed by Contractor | Percent Incinerated | = | Quantity Incinerated |
| (537 kkg | - | 80.6 kkg) | (0.65) | (0.05) | = | 14.8 kkg |

| | | | |
|---|---|---|---|
| Quantity of Methyl Chloroform Incinerated | 1-Incineration Efficiency | = | Air Emissions of Methyl Chloroform from Incineration |
| (14.8 kkg) | (1-0.95) | = | 0.740 kkg |

| | | | |
|---|---|---|---|
| Quantity of Methyl Chloroform Incinerated | Incineration Efficiency | = | Quantity of Methyl Chloroform Destroyed |
| (14.8 kkg) | (0.95) | = | 14.1 kkg |

| | | | | | | |
|---|---|---|---|---|---|---|
| Quantity of Solvent Used in Cleaning | - | Quantity Emitted to Air | Percent Reclaimed In-house | Efficiency of Solvent Recovery | = | Quantity Reclaimed In-house |
| (537 kkg | - | 80.6 kkg) | (0.15) | (0.9) | = | 61.6 kkg |

| | | | | | | |
|---|---|---|---|---|---|---|
| Quantity of Solvent Used in Cleaning | - | Quantity Emitted to Air | Percent Reclaimed In-house | Percent Landfilled | = | Quantity Landfilled |
| (537 kkg | - | 80.6 kkg) | (0.15) | (0.1) | = | 6.85 kkg |

| | | | | | |
|---|---|---|---|---|---|
| Quantity of Solvent Used in Cleaning | - | Quantity Emitted to Air | Percent Discharged | = | Quantity Discharged |
| (537 kkg | - | 80.6 kkg) | (0.20) | = | 91.3 kkg |

It is assumed that 95% of the quantity discharged (86.7 kkg) will evaporate and the remaining 4.27 kkg will remain in water.

The percents of methyl chloroform released or reclaimed are estimated to have the uncertainties shown in Table 3.3-3 also shows overall uncertainties which have accounted for an uncertainty estimate of +30% and -50% for the total methyl chloroform used to clean vessels from water based adhesive formulations.

Table 3.3-3 Summary of Uncertainties for Environmental Releases from Vessel Cleaning

| Source | Quantity (kkg) | Percentage of Individual Uncertainty (%) | Percentage of Overall Uncertainty (%) |
|---|---|---|---|
| Quantity Emitted to Air | 80.6 | ±25 | +39/-56 |
| Quantity Reclaimed by Outside Contractor | 282 | +10/-30 | +40/-64 |
| Quantity of Still Bottoms Incinerated | 14.8 | +10/-30 | +40/-64 |
| Incinerator Air Emissions | 0.740 | ±80 | +89/-100 |
| Methyl Chloroform Destinction (Incineration) | 14.1 | ±4 | +40/-64 |
| Quantity Reclaimed In-house | 61.6 | ±25 | +46/-61 |
| Quantity of Still Bottoms Landfilled | 6.85 | ±25 | +46/-61 |
| Quantity Discharged | 91.3 | +30/-10 | +49/-57 |

### 3.3.4.2 Solvents for Emulsions

It is assumed that all other losses of methyl chloroform occur in the formulation and end use of emulsion adhesives.

These losses can be estimated using the following equation.

| Total Methyl Chloroform Used in Adhesives Industry | - | Quantity Used for Solvent Based Adhesives | + | Quantity Used For Cleaning Vessels for Water-based Adhesives | = | Total Solvent Used for Water-Based Emulsions |
|---|---|---|---|---|---|---|
| (19,800 kkg) | - | (16,700 kkg | + | 537 kkg) | = | 2,560 kkg |

Since this estimate is the difference between total solvent used in the adhesives industry and the losses from solvent based adhesives plus water based adhesives vessel cleaning there is a large uncertainty associated with this value. JRB estimates the uncertainty to be ±75%.

Of the total methyl chloroform lost from water based emulsions, an estimated 0.5 percent is lost during production (Hall, J., 1979; Wilholdt Cement, 1979). JRB considers this estimate to be accurate to +50% and -20%.

| Methyl Chloroform Emissions from Water-based Emulsions | Percent Lost During Production | = | Quantity Lost During Production |
|---|---|---|---|
| (2.560 kkg) | (0.005) | = | 12.8 kkg |

Considering the uncertainty estimate of ±75 percent for total solvent releases from end products, the overall uncertainty is estimated at +90% and -78%.

The remaining 2,550 kkg are lost during end-use of emulsion based adhesives. Assuming that 95 percent is emitted to air from the use of these adhesives and 5 percent is landfilled as residue in containers, releases to air and land are estimated as follows:

(Releases from Use of Water Based Adhesives) (Percent Emitted to Air) = Quantity Emitted to Air

(2,550 kkg) (0.95) = 2,420 kkg

(Releases from Use of Water Based Adhesives) (Percent Landfilled) = Quantity Landfilled

(2.550 kkg) (0.05) = 128 kkg

JRB's estimate for the percent released to air and land are considered accurate to ±15% and ±75% respectively. Accounting for the uncertainty estimate of ± 75% for the quantity used in solvent based adhesives, the overall uncertainties are estimated to be ±76% for releases to air and +106% and -99% percent for releases to land.

The results of this analysis, shown in Figure 3.3-2 suggest that 91 percent of the total solvent losses are from end uses. Three percent is reclaimed by contractors and sold for other uses. Only one percent of the solvent is emitted directly to the atmosphere from the process and 3 percent is discharged to wastewater treatment systems. Less than one percent of the solvent is lost by landfilling or destroyed by incineration.

### 3.3.5 Multimedia Environmental Losses

Figure 3.3-4 summarizes the environmental releases of methyl chloroform from the production and use of adhesives.

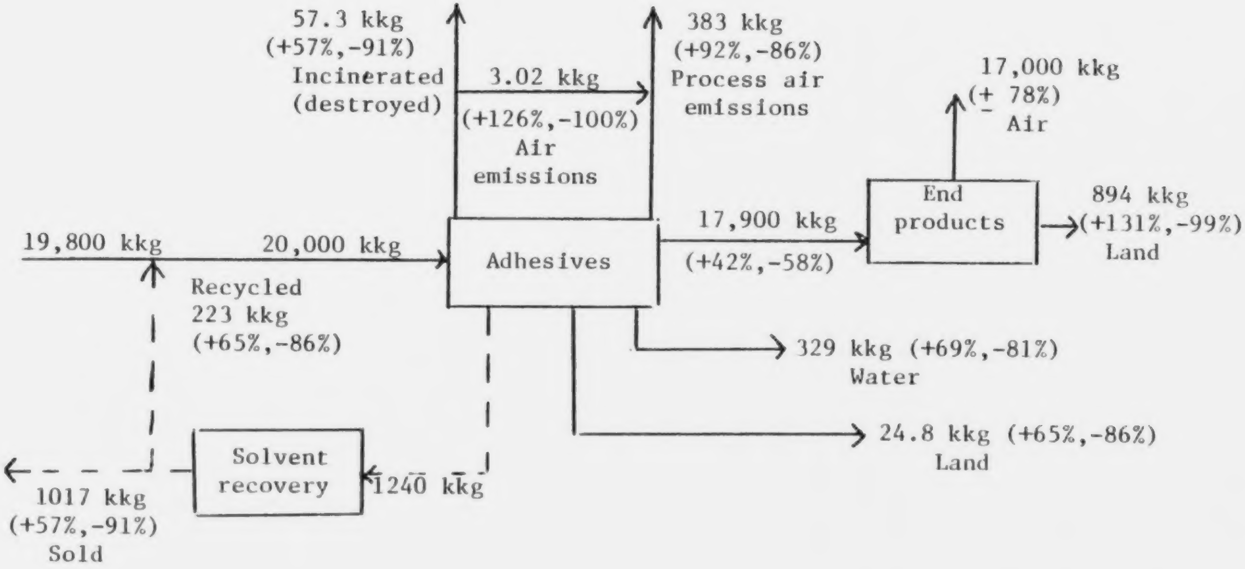

57.3 kkg
(+57%,-91%)
Incinerated
(destroyed)
3.02 kkg
(+126%,-100%)
Air
emissions
383 kkg
(+92%,-86%)
Process air
emissions
17,000 kkg
(± 78%)
Air
19,800 kkg
20,000 kkg
Adhesives
17,900 kkg
(+42%,-58%)
End
products
894 kkg
(+131%,-99%)
Land
Recycled
223 kkg
(+65%,-86%)
329 kkg (+69%,-81%)
Water
24.8 kkg (+65%,-86%)
Land
Solvent
recovery
1240 kkg
1017 kkg
(+57%,-91%)
Sold

Figure 3.3-4 Total Multimedia Environmental Losses from the Formulation and Use of Adhesives

## 3.4 TEXTILES

### 3.4.1 Use and Quantification of Methyl Chloroform in Textiles

Methyl chloroform is used in the textile industry as a cleaning and scouring solvent, and as a dye carrier. There is little information on the quantity of methyl chloroform used in these applications. Contact with various textile trade associations and dye carrier manufacturers did not yield a significant amount of information detailing the use of methyl chloroform by the textile industry.

Millions of pounds of methyl chloroform are used in the textile industry as a scouring solvent for wool and knit material, but the quantity used in the dye carrier business is negligible (Perkins, 1979). Contacts with various dye carrier producers indicated that methyl chloroform is not used extensively as a dye carrier. They also suggested that the quantity of methyl chloroform used in the production of dye carrier in 1978 could have been as high as 10 kkg (Piedmont, 1979; Tanatex, 1979). Thus, it is assumed that the use of methyl chloroform in the textile industry is primarily as a scouring and cleaning solvent.

A flow diagram of the quantity of methyl chloroform used in the textile industry is shown in Figure 3.4-1.

### 3.4.2 Emissions of Methyl Chloroform from the Production of Textiles

A total of 1973 establishments that perform dyeing and/or finishing operations were identified as potential sources of hazardous pollutant releases (EPA, 1976; EPA, 1979d). These textile establishments were divided into the subcategories presented in Table 3.4-1.

Of these subcategories, methyl chloroform has been identified in the effluent of subcategories 1, 4, and 5 where much of the scouring work is performed (EPA, 1979d). Monitoring data obtained for the textile mills in subcategories 1, 4, and 5 revealed that methyl chloroform was present at an average level of 7mg/l, with a maximum level of use of 17mg/l (EPA, 1979).

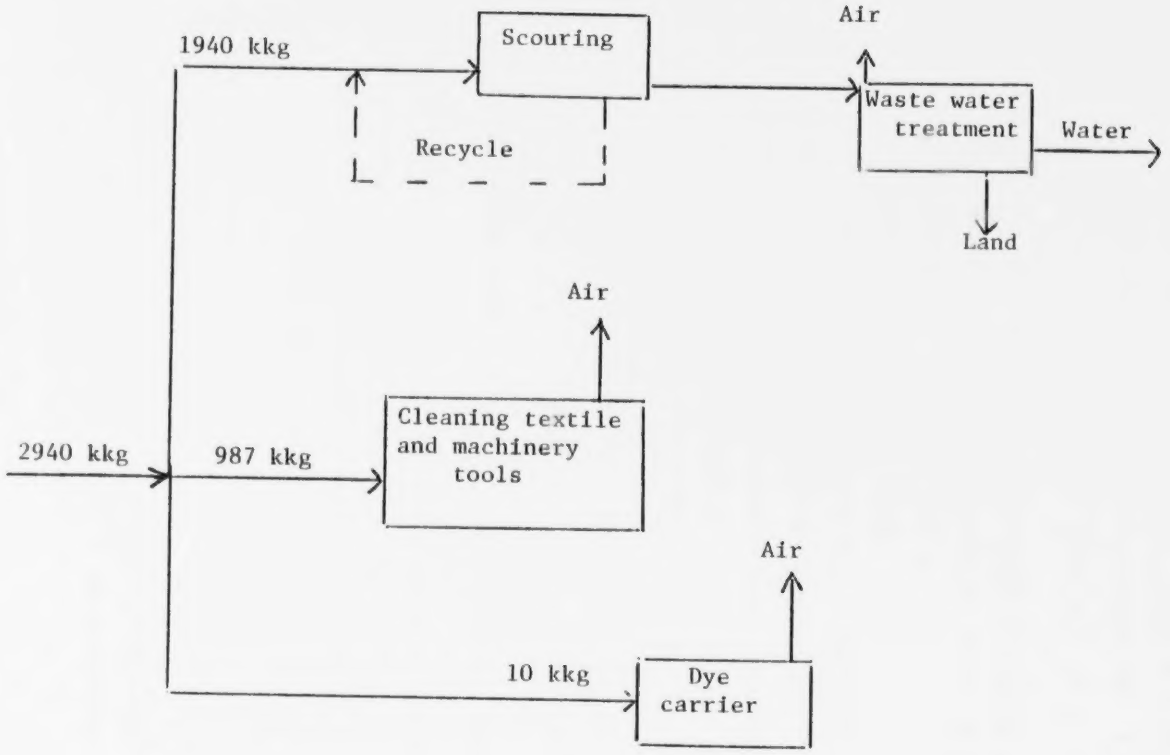

1940 kkg
Scouring
Recycle
Air
Waste water treatment
Water
Land
Air
2940 kkg
987 kkg
Cleaning textile and machinery tools
Air
10 kkg
Dye carrier

Figure 3.4-1 Flow Diagram of Methyl Chloroform Used in Textiles *

* Numbers may not add due to rounding

Table 3.4-1 Subcategories of the Textile Industry

| Subcategories | | Number of Plants |
|---|---|---|
| 1. | Wool Scouring | 17 |
| 2. | Wool Finishing | 37 |
| 3. | Low Water Use Processing | 808 |
| 4. | Woven Fabric Finishing | 336 |
| 5. | Knit Fabric Finishing | 282 |
| 6. | Hosiery Finishing | 160 |
| 7. | Carpet Finishing | 58 |
| 8. | Stock and Yarn Finishing | 217 |
| 9. | Non-woven Manufacturing | 38 |
| 10. | Felted Fabric Processing | 20 |
| | Total | 1,973 |

Source, EPA, 1979d

According to a survey done by the Institute of Textile Technology, a textile plant uses approximately 100 lbs/month, or 0.54 kkg per year, of methyl chloroform (Barhorsky, 1979). An uncertainty of +50%, -30%, was attached to this estimate, due to the degree of error inherent in surveys, the varying size and production capacities of scouring plants, the different methods of scouring employed, and the substitution of other scouring solvents (perchloroethylene, trichloroethylene). Because this survey was performed by an organization primarily concerned with the production process of textiles, it is assumed that this quantity is used for cleaning textile machinery and tools. Survey information provided by an industry official described the annual use of 720 gallons (3.6 kkg) of methyl chloroform in textile establishment (Owenbey, 1979). An uncertainty of ±30% is assigned to this estimate, due to the error inherent in surveys. Based on the fact that this amount of use covers all operations of a typical textile plant, it is assumed that this quantity of methyl chloroform is consumed for both scouring and cleaning.

In accordance with the above assumptions, the amount of methyl chloroform used for scouring in a textile plant can be calculated as follows:

| | | | | |
|---|---|---|---|---|
| Amount of Methyl Chloroform Used Scouring and Cleaning | - | Amount of Methyl Chloroform Used For Cleaning | = | Amount of Methyl Chloroform Used For Scouring |
| 3.6 kkg | - | 0.54 kkg | = | 3.06 kkg |

The uncertainty of the amount of methyl chloroform used for scouring is +58%, -42%, because of the uncertainty of the amount of methyl chloroform used for scouring and cleaning (±30%) and the uncertainty of the amount of methyl chloroform used for cleaning (±50, -30%).

The total number of plants involved in scouring operations, as indicated by subcategories 1, 4, and 5 in Table 3.4-1, is 635. The uncertainty of this total is ±10%, because data documenting the type of operations performed in textile plants is available. Accordingly, the total amount of methyl chloroform used for scouring in the textile industry can be calculated as follows:

| | | | |
|---|---|---|---|
| Total Number of Plants Involved in Scouring Operation | Annual Amount of Methyl Chloroform Used for Scouring Per Plent | = | Total Number of Methyl Chloroform Used for Scouring |
| (635) | (3.06 kkg) | = | 1,940 kkg |

The uncertainty of the annual amount of methyl chloroform used for scouring is +59%, -43%, due to the uncertainty of the total number of plants involved in scouring operations (±10%) and the uncertainty of the annual amount of methyl chloroform used for scouring (+58%, -42%).

3.4.2.1 Emissions Due to Textile Scouring

Based on the analysis of available data, it was determined that a majority of the textile plants recycle their solvents. The recycle efficiency has been estimated at 95 percent (±2%) (Bahorsky, 1979). A simplified diagram of the scouring system is as follows:

38,800 kkg

Scouring

1,940 kkg
(wastewater)

Recycle
36,900 kkg

Due to the high efficiency of the solvent recovery system, it was assumed that there were no air emissions of methyl chloroform during the scouring process (Bahorsky, 1979). An uncertainty of +71%, -59% for the quantity of solvent used for scouring and the amount of methyl chloroform recycled due to the reliability of recycle efficiencies.

### 3.4.2.1.1 Emissions to Air from Wastewater Treatment

As stated above, 1,940 kkg of methyl chloroform is assumed to be discharged to the wastewater of textile plants. During wastewater treatment, the following steps occur: a) preliminary wastewater treatment, b) aeration and/or activation of sludge, and c) secondary wastewater treatment. Based on the high volatility of methyl chloroform, it is assummed that 99 percent of the total amount present in the wastewater is evaporated during the aeration/activation of the sludge. An uncertainty of +0.75%, -1%, was assigned to this assumption, due to the empirical nature of methyl chloroform's volatility and the high degree of agitation obtained during aeration/activation of sludge. The amount of mehtyl chloroform volatilized during aeration can be calculated as follows:

| Amount of Methyl Chloroform in Wastewater | Percent of Methyl Chloroform Volatilized | = | Amount of Methyl Chloroform Volatilized |
|---|---|---|---|
| (1,940 kkg) | (0.99) | = | 1,920 |

The uncertainty of the amount of methyl chloroform volatilized is +59%, -43%, due to the uncertainty of the amount of methyl chloroform discharged to the wastewater (+59%, -43%), and the uncertainty of the percent of methyl chloroform volatilized (+0.75%, -1%).

### 3.4.2.1.2 Emission to Water after Wastewater Treatment

Of the remaining 1 percent, it is assumed that 10 percent and 90 percent are dissolved in the effluent and absorbed in the sludge, respectively. These assumptions are based on the solubility of mehtyl chloroform in water (1,300 ppm) and the low degree of methyl chloroform biodegradation by microorganisms (Section 2.6). An uncertainty of ±20% is assigned to these percentages, which reflects the empirical nature of both of these assumptions.

The amount of methyl chloroform dissolved in the wastewater effluent can be calculated as follows:

| Amount of Methyl Chloroform Discharged to Wastewater | Percent of Methyl Chloroform Dissolved | = | Amount of Methyl Chloroform in Wastewater |
|---|---|---|---|
| (1,940 kkg) | (0.001) | = | 1.94 kkg |

The uncertainty of the amount of methyl chloroform dissolved in wastewater effluent is +62%, -47%, because the uncertainty of the amount of methyl chloroform discharged to the wastewater is +59%, -43%, and the uncertainty of the percent of methyl chloroform dissolved is ±20%.

The average concentration of methyl chloroform in the aqueous effluent of a textile scouring plant can be calculated based on the following assumptions:

- Total annual amount of methyl chloroform discharged in effluent: 1.94 kkg;
- Total number of textile scouring plants: 635;
- Average rate of water discharge from a textile scouring plant: $1.56 \times 10^8$ liters/yr (EPA, 1979d).

As discussed earlier, the uncertainty of the amount of methyl chloroform discharged in the effluent is +62%, -47%, while the uncertainty of the total number of textile scouring plants is ±10%. The uncertainty of the average rate of water discharge from a textile scouring plant is ±25%, due to the error inherent in averaging calculations. Accordingly, the average concentration of methyl chloroform in the effluent can be calculated as follows:

$$\frac{\text{Annual Amount of Methyl Chloroform Discharged in Effluent}}{\text{Number of Textile Scouring Plants}} = \text{Average Quantity of Methyl Chloroform Discharged by One Textile Scouring Plant}$$

$$\frac{1.94 \text{ kkg}}{635} = 0.00306 \text{ kkg/plant/year}$$

$$= 3.06 \times 10^{3} \text{ g/plant/year}$$

$$\frac{\text{Average Annual Quantity of Methyl Chloroform by One Textile Scouring Plant}}{\text{Average Rate of Water Discharged From a Textile Scouring Plant}} = \text{Average Concentration of Methyl Chloroform in Aqueous Effluent of a Textile Scouring Plant}$$

$$\frac{3.06 \times 10^{3} \text{ g/plant/yr}}{1.56 \times 10^{8} \text{ liters/plant/yr}} = 19.5\ \mu\text{g/liter}$$

The uncertainty of the average concentration of methyl chloroform in the aqueous effluent is +66%, -52%, due to the uncertainties of the assumptions stated earlier.

### 3.4.2.1.3 Emission to Land from Wastewater Sludge

As stated earlier, 90 percent of the methyl chloroform not volatilized during wastewater treatment is absorbed by the wastewater sludge. Therefore, the amount of methyl chloroform absorbed in the wastewater sludge can be calculated as follows:

| Amount of Methyl Chloroform Discharged in Wastewater | Percent of Methyl Chloroform Absorbed in Sludge | = | Amount of Methyl Chloroform Absorbed in Wastewater Sludge |
|---|---|---|---|
| (1,940 kkg) | (0.009) | = | 17.5 kkg |

The uncertainty of the amount of methyl chloroform absorbed in the wastewater sludge is +62%, -47%, due to the amount of methyl chloroform discharged to the wastewater (+59%, -43%) and the uncertainty of the percent of methyl chloroform absorbed in the sludge (±20%).

### 3.4.2.2 Emission Due to Cleaning Textile Machinery and Tools

According to Bahorsky, methyl chloroform and other chlorinated solvents are also used as cleaning solvents for textile machinery and tools, such as fiber spools (Bahorsky, 1979). However, quantitative information to substantiate this statement was not available. Therefore, it was assumed that 0.5 kkg of methyl chloroform is consumed per year by a typical textile plant. Because this assumption is not based on any corroborating data an uncertainty of ± 95% was assumed. These assumptions should be verified in later studies.

As stated earlier, 1,973 textile plants were identified as solvent users by EPA (EPA, 1979d). An uncertainty of ±10% was assigned to this number, for reasons stated earlier with regard to the number of textile scouring plants in this country. The amount of methyl chloroform used for cleaning can be calculated as follows:

| Number of Textile Textile Plants Using Solvents | Annual Amount of Methyl Chloroform Used per Plant | = | Total Amount of Methyl Chloroform Used for Cleaning by Textile Industry |
|---|---|---|---|
| (1,973) | (0.5 kkg) | = | 987 kkg |

The uncertainty of the amount of methyl chloroform used by the textile industry is ±96%, due to the uncertainty of the number of textile plants (±10%) and the uncertainty of the annual amount of methyl chloroform used per plant (±95%).

Investigations conducted by JRB did not reveal the use of air and water emission controls during cleaning operations. Therefore, it was assumed that 100 percent (+0%, -5%) of the methyl chloroform used for cleaning was volatilized. This estimate is based on the empirical nature of methyl chloroform's volatility. The possibility that some methyl chloroform volatilized during cleaning operations can be calculated as follows:

| Amount of Methyl Chloroform Used for Cleaning | Percent of Methyl Chloroform Volatilized During Cleaning | = | Amount of Methyl Chloroform Volatilized During Cleaning Operations |
|---|---|---|---|
| (987 kkg) | (1.0) | = | 987 kkg |

The uncertainty of the amount of methyl chloroform volatilized during cleaning is ±96% due to the uncertainty of the amount of methyl chloroform used for cleaning (±96%) and the uncertainty of the percent of methyl chloroform volatilized during cleaning (+0%, -5%).

### 3.4.2.3 Emission Due to Use as a Dye Carrier

As stated earlier in Section 3.4.1, an estimate of 10 kkg was obtained for the use of methyl chloroform as a dye carrier. An uncertainty of ±50% is assigned to this estimate, due to its reliance on verbal communications. In conversations with industry officials, it was established that measures are not used to control the air emission of solvents during their use in textile material dyeing operations (Owenbey, 1979). Therefore, it was assumed that 100 percent of all methyl chloroform used as a dye carrier is volatilized, discounting the minimal amount that is absorbed on the dyed material (Owenbey, 1979; Tanatey, 1979; Bahorsky, 1980). This assumption is based on the volatility of methyl chloroform and the nature of its use during dyeing operations. An uncertainty of ±25% was assigned to this assumption, based on the measured value of methyl chloroform's volatility. The amount of methyl chloroform volatilized during dyeing operations can be calculated as follows:

| Amount of Methyl Chloroform Used in Dyeing Operations | Percent of Methyl Chloroform Volitilized During Dyeing Operations | = | Amount of Methyl Chloroform Volatilized During Dyeing Operations |
|---|---|---|---|
| (10 kkg) | (1.0) | = | 10 kkg |

The uncertainty of the amount of methyl chloroform volatilized during dyeing operations is ±56% due to the uncertainty of the amount of methyl chloroform used in dyeing operations (±50%) and the uncertainty of the percent of methyl chloroform volatilized (±25%).

### 3.4.3 Multimedia Environmental Losses

Figure 3.4-2 summarizes the environmental release of methyl chloroform from the production of textiles.

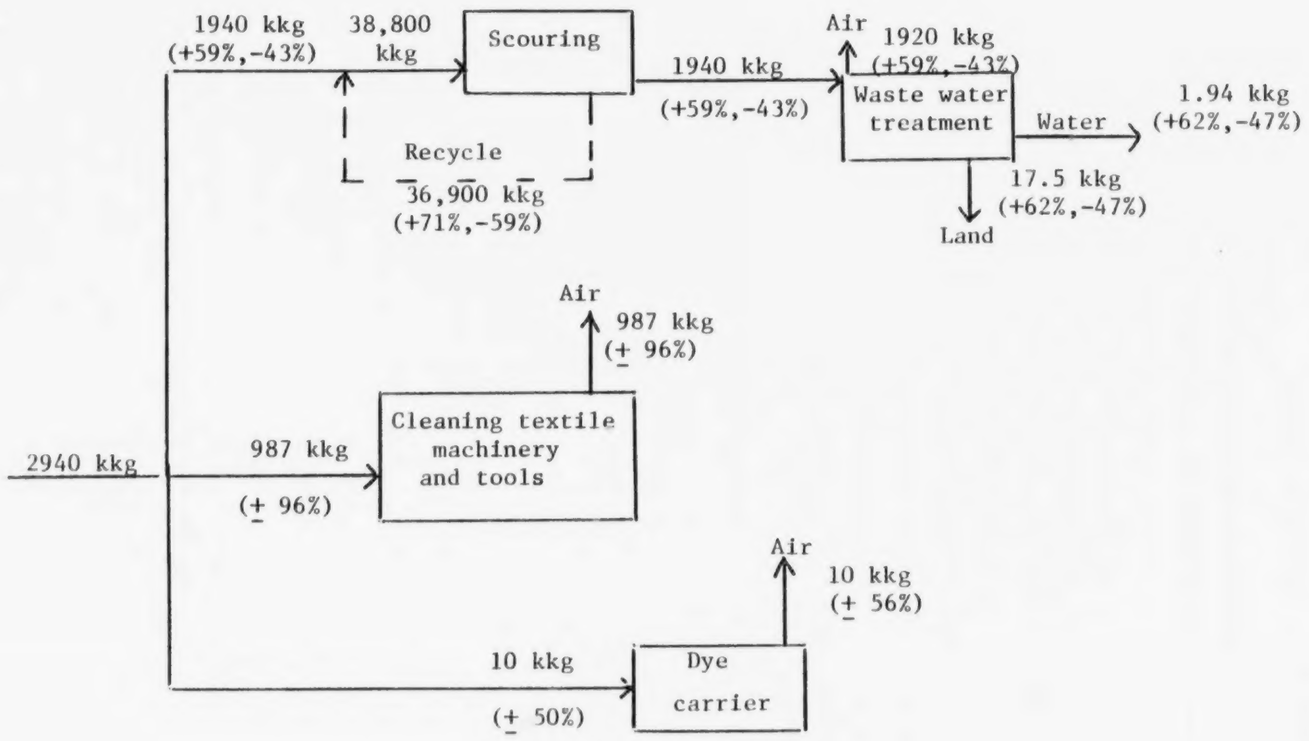

1940 kkg
(+59%,-43%)
38,800
kkg
Scouring
Recycle
36,900 kkg
(+71%,-59%)
1940 kkg
(+59%,-43%)
Air
1920 kkg
(+59%,-43%)
Waste water
treatment
Water
1.94 kkg
(+62%,-47%)
17.5 kkg
(+62%,-47%)
Land
2940 kkg
987 kkg
(± 96%)
Cleaning textile
machinery
and tools
Air
987 kkg
(± 96%)
10 kkg
(± 50%)
Dye
carrier
Air
10 kkg
(± 56%)

Figure 3.4-2 Multimedia Environmental Losses of Methyl Chloroform from Textiles

## 3.5 DRAIN CLEANERS AND SEPTIC TANK CLEANERS

### 3.5.1 Use of Methyl Chloroform in Drain and Septic Tank Cleaners

Organic solvent based drain cleaners and septic tank cleaners are intended to alleviate drains and pipes clogged by grease. These products usually contain petroleum distillates, namely methylene chloride, methyl chloroform and/or orthodichlorobenzenes. (Chem. Week, 4/79; Nassau County Health Dept., 1979). Concern over the use of these products arose when high concentrations of methyl chloroform were found in the groundwater of Nassau County, NY. A Nassau County Consumer Product Survey identified 12 solvent based cleaners, 4 of which contained methyl chloroform. The survey determined that in 1977 there were 100 kkg of methyl chloroform sold in Nassau County alone in septic tank cleaners and drain cleaner products. Two septic tank cleaners manufactured by one company accounted for 80 percent of the sales (Nassau County Health Dept., 1979).

Following the identification of high levels of methyl chloroform in Nassau County groundwater in 1977, those drain cleaning products making up 20 percent of methyl chloroform sold in drain cleaners and septic tank cleaners combined were removed from the market (Chem. Week, 4/79; Nassau County Health Dept., 1979). It is not known if these products were removed from markets in other geographic areas as well. However, the septic tank cleaners, representing 80 percent of the methyl chloroform sales in this product category, remained on the market throughout 1978. The manufacturers of these products claim to have changed their formulation recently, but no analysis is yet available (P. Skinner, 1979).

An accurate estimate of the nationwide sales of these products would require that a consumer product survey be conducted nationwide or that proprietary sales data be released. Neither method was feasible within the scope or time-frame of this study.

It is known however that sales of these products in Nassau County, Long Island are not representative of sales nationwide. The following information suggests that these products were not so widely used nationwide in 1978 as they were in Nassau County.

- Municipal Environmental Research Labs (MERL) was not aware of these products being used extensively outside the east coast, with the possible exception of commercial establishments (by phone J. Kreissel, MERL, 1979).
- The N.Y. State Attorney General's Office found, that although septic tank cleaners were sold in upstate N.Y., sales volume was considerably lower than in Nassau County (P. Skinner, 1979). These products were known to be used in Cape Cod, Connecticut and Florida although the quantities used are not known (P. Skinner, 1979).
- Several septic tank cleaning services in the Washington Metropolitan area were contacted about the use of solvent based cleaners. While some indicated that the solvent based cleaners were probably sold, caustic type cleaners were far more frequently used (Americana, Great Falls, and Fairfax Septic Tank Services, 1979; Suburban Sanitary Engineers, 1979).

### 3.5.2 Quantification of Methyl Chloroform Used in Drain and Septic Tank Cleaners

Total methyl chloroform used in solvent based drain cleaners and septic tank cleaners in 1978 was estimated at 1,500 kkg or 0.5 percent of total methyl chloroform produced. This estimate was made by assuming a "reasonable use" of these products among homeowners in eastern states. Since this estimate is not based on actual end use data, it is not expected to be more accurate than +75 and -50%. The estimate for septic tank cleaners assumed that in 1978, 30 percent of homeowners with septic tanks experienced drainage problems or took precautionary measures to avoid these problems. This is based on health department and septic tank services recommendations that septic tanks at homes with garbage disposals should be pumped annually and those without garbage disposal should be pumped every 3-5 years (Fairfax County Health Dept., 1979; Great Falls and Fairfax Septic Tank Services, 1979). Since a majority of homeowners do not have their tank pumped until they have problems, it seems reasonable to estimate drainage problems at 30 percent for an upper limit. Such problems almost invariably occur every 1-1.5 years where a garbage disposal is used (Great Falls and Fairfax Septic Tank Services, 1979), although homeowners without a garbage disposal may go 10 years without problems. It was also assumed that only 10 percent of the homeowners with drainage problems used solvent based cleaners, and that 90 percent used caustic cleaners or immediately called for the services of a plumber or septic tank cleaner.

It was assumed that these products were sold to an estimated population of 90 x $10^6$ in the eastern states of: New York, New Jersey, Pennsylvania, Connecticut, Rhode Island, Massachusetts, Delaware, Maryland, Florida, Georgia, Virginia, and Ohio. About twenty-five percent of the homes are estimated to have septic tanks (based on a national average) (Hammer, 1975). If we estimate an average household size of 3.0 for homes served by sewers and 4.0 for homes without sewers, then, the number of homes with septic tanks is estimated as follows:

$$\text{Population of Eastern States} = \text{Residents per Household in Sewered Homes} \times \text{Percent with Sewers} \times \text{No. of Households with Sewers} + \text{Residents per Household with Septic Tanks} \times \text{Percent with Septic Tanks} \times \text{No. of Households on Septic Tanks}$$

$$(90 \times 10^6 \text{ residents}) = \left(3\ \frac{\text{residents}}{\text{homes}}\ (.75\,x)\right) + \left(4\ \frac{\text{residents}}{\text{homes}}\ (.25\,x)\right)$$

$0.75x = 20.5 \times 10^6$ homes on sewers

$0.25x = 6.9 \times 10^6$ homes with septic tanks

We assumed that 30 percent of home owners with septic tanks experienced drainage problems in 1978. Ten percent of these tried to "unclog" the system with solvent based cleaners or took precautionary measures to avoid these problems by using solvent cleaners and 90 percent used caustic cleaners or immediately called for services of a plumber or a septic tank service. It was also estimated that 30 percent of total solvent used was methyl chloroform (based on Nassau County Consumer Product Survey, 1978) and that homeowners used two applications of a full 7.5 liter (2.0 gal.) dose. Total methyl chloroform used by homes with septic tanks was then estimated as follows:

| No. of Homes with Septic Tanks | Percent with Drainage Problems | Percent Using Solvent Cleaners | Percent Methyl Chloroform in Cleaners |
|---|---|---|---|
| ($6.9 \times 10^6$ homes) | (.3) | (.1) | (.3) |

| Volume of Cleaner | = | Volume of Methyl Chloroform Used |
|---|---|---|
| (15 liters/home) | = | $93 \times 10^4$ liters |

Since the density of methyl chloroform is 1.32 g/ml, then the quantity of methyl chloroform used equals

$$93 \times 10^4 \text{ liters} \times 1.32 \text{ kg/liter} = 1200 \text{ kkg}$$

This estimate corresponds to an annual average household use of 0.2 kg. Average household use of methyl chloroform in septic tank cleaning products in Nassau County was 0.7 kkg/household or a full 2 gallon "dose" used by 22 percent of the homes with septic tanks. Estimates of methyl chloroform used in drain cleaners alone were made by assuming that they represent 25 percent of the quantity of methyl chloroform used in septic tank cleaners (based on Nassau County Survey).

| Quantity Used in Septic Tank Cleaners | Percent of This Quantity Used in Drain Cleaners | = | Total Methyl Chloroform in Drain Cleaners |
|---|---|---|---|
| (1200 kkg) | (.25) | = | 300 kkg |

The total quantity used in drain cleaners is then estimated as follows:

| Quantity Used in Septic Tank Cleaners | + | Quantity Used in Drain Cleaners | = | Total Methyl Chloroform Used |
|---|---|---|---|---|
| (1200 kkg) | + | (300 kkg) | = | 1500 kkg |

### 3.5.3 Multimedia Environmental Losses

Figure 3.5-1 shows multimedia environmental losses of methyl chloroform from drain cleaners and septic tank cleaners assuming that 1978 losses amounted to 1,500 kkg or 0.5 percent of the total methyl chloroform.

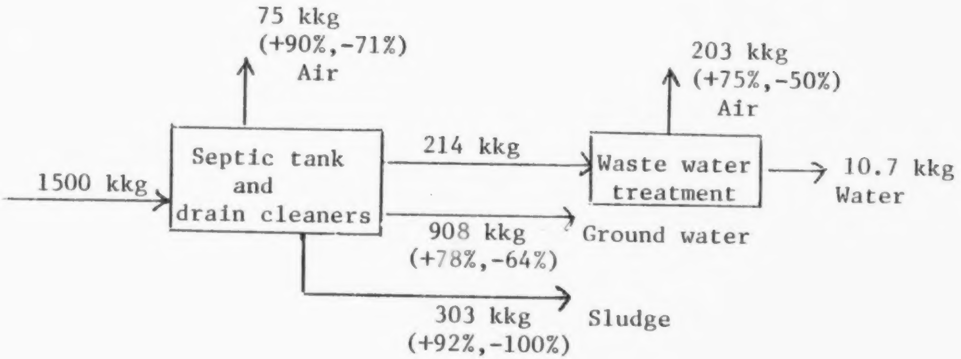

75 kkg
(+90%,-71%)
Air
1500 kkg
Septic tank
and
drain cleaners
214 kkg
Waste water
treatment
203 kkg
(+75%,-50%)
Air
10.7 kkg
Water
908 kkg
(+78%,-64%)
Ground water
303 kkg
(+92%,-100%)
Sludge

Figure 3.5-1 Multimedia Environmental Losses of Methyl Chloroform from Septic Tank Cleaners and Drain Cleaners

### 3.5.3.1 Multimedia Environmental Releases from Septic Tank Cleaners

Since methyl chloroform is denser than water, it sinks to the bottom of the septic tank. The solvent then acts by dissolving the sludge. The dissolved or semi-dissolved sludge containing methyl chloroform can then pass into the leachfield with the water, thereby contaminating the groundwater. Often the chemically treated sludge gets stuck in the pipe leading to the leachfield and a plumber's services are required (Suburban Sanitary Engineers, 1979; Fairfax County Health Dept., 1979).

To determine multimedia environmental losses from septic tank cleaners, it was assumed the 5 percent of the solvent is lost by evaporation. Of the solvent discharged to the septic tank, it was assumed that 25 percent remains in the sludge and is lost by evaporation when the septic tank is pumped. The other 75 percent is discharged to the groundwater. Methyl chloroform does not degrade in the groundwater and will be lost from this media only when the water is pumped for consumptive or non-consumptive uses. These assumptions need to be confirmed by further study. The distribution of methyl chloroform between air, sludge and groundwater is estimated as follows:

| Total Methyl Chloroform in Septic Tank Cleaners | Percent Evaporated | = | Quantity of Methyl Chloroform Evaporated |
|---|---|---|---|
| (1200 kkg) | (0.05) | = | 60 kkg |

Releases to sludge and groundwater are similarly estimated by multiplying the total methyl chloroform in septic tank cleaners by the percent released to groundwater or sludge.

| Methyl Chloroform in Septic Tank Cleaners | - | Quantity of Methyl Chloroform Evaporated | Percent Retained in Sludge | = | Quantity of Methyl Chloroform Retained in Sludge |
|---|---|---|---|---|---|
| (1200 kkg | - | 60 kkg) | (0.25) | = | 285 kkg |

| Methyl Chloroform in Septic Tank Cleaners | - | Quantity of Methyl Chloroform Evaporated | Percent Released to Groundwater | = | Quantity of Methyl Chloroform in Groundwater |
|---|---|---|---|---|---|
| (1200 kkg | - | 60 kkg) | (0.75) | = | 855 kkg |

These estimates are not based on actual data and should be verified in later studies. Our estimate for the percent released to air is probably accurate to ±50%. The estimate for percent released to groundwater is considered accurate to +20% and -40% and releases to sludge have an uncertainty of +60% and -100%. Accounting for the uncertainty of +75% and -50% for the quantity of methyl chloroform used in drain cleaners and septic tank cleaners our overall uncertainties are:

- +90% and -71% for releases to air
- +92% and -100% for releases to sludge
- +78% and -64% for releases to groundwater

### 3.5.3.2 Multimedia Environmental Releases from Drain Cleaners

Drain cleaning products are used in sewered and unsewered areas alike. It is assumed that 75 percent of the drain cleaners are used by homeowners served by sewers (based on national percentage of homes with sewers), that 5 percent (±80%) of the solvent losses are due to evaporation and 95 (±4%) percent is discharged to municipal treatment systems, where the solvent is largely evaporated prior to stream discharge.

For homeowners with septic tanks, the quantity of methyl chloroform lost to groundwater and the quantity retained in sludge is assumed to be similar to those estimates for septic tank cleaners. Based on these assumptions, releases of methyl chloroform from the use of drain cleaners are estimated as follows:

#### Releases from Homes with Sewers

| Quantity of Methyl Chloroform in Drain Cleaners | Percent Used by Sewered Homes | = | Quantity of Methyl Chloroform Used by Sewered Homes |
|---|---|---|---|
| (300 kkg) | (0.75) | = | 225 kkg |

Quantity Evaporated:

(225 kkg)(0.05) = 11.3 kkg

Quantity Discharged:

(225 kkg)(0.95) = 214 kkg

Accounting for uncertainties related to total methyl chloroform used in drain cleaners (+75% and -50%) and the quantities evaporated and discharged, overall uncertainty estimates are +75% and -53% for the quantity discharged and +110% and -94% for releases to air. It is assumed that about 95 percent of the quantity discharged (203 kkg) will volatilize before stream discharge and the remaining 10.7 kkg will remain in the water.

### Releases from Homes with Septic Tanks

The remaining 25 percent of the methyl chloroform released from drain cleaners was used by homes with septic tanks.

| Quantity of Methyl Chloroform in Drain Cleaners | Percent of Homes with Septic Tanks | = | Quantity of Methyl Chloroform used by Homes with Septic Tanks |
|---|---|---|---|
| (300 kkg) | (0.25) | = | 75 kkg |

Assuming the solvent is released similarly to the release pattern for septic tank cleaners, then:

Quantity Evaporated:

(75 kkg)(0.05) = 3.75 kkg

Quantity Released to Sludge:

(75 kkg - 3.75 kkg)(.25) = 18 kkg

Quantity Released to Groundwater:

(75 kkg - 3.75 kkg)(.75) = 53 kkg

Overall uncertainties for these estimates are:

- +90% and -71% for releases to air;
- +96% and -100% for releases to sludge;
- +78% and -64% for releases to groundwater.

## 3.6 PAINTS

The use of methyl choroform in the paints industry was investigated. It has been identified as a solvent raw material for the formulation of paints (EPA, 1979e). However, additional quantitative date regarding the amount of use was unavailable. Conversations with industry officials revealed that it is used as a solvent in traffic paint formulations (Moen, 1979; Nolt, 1979). In a conversation with a trade association official, it was determined that methyl chloroform comprised no more than 1 percent of the total amount of aliphatic hydrocarbons used by the paint industry. This official estimated the total amount of aliphatic hydrocarbons used by the paint industry at 500,000 kkg (Benedict, 1979). Due to the gross nature of these estimates, and lack of any additional substantive data, an uncertainty of ±75% was estimated for these assumptions. The amount of methyl chloroform used in the paints industry can be calculated as follows:

| Amount of Aliphatic Hydrocarbons Used in Paints Industry | Methyl Chloroform Percentage of Total Amount of Aliphatic Hydrocarbons | = | Amount of Methyl Chloroform Used in Paints Industry |
|---|---|---|---|
| (500,000 kkg) | (0.01) | = | 5,000 kkg |

The uncertainty of the amount of methyl chloroform used by the paints industry is +106%, -99%, due to the ±75% uncertainties of the total amount of aliphatic hydrocarbons used and methyl chloroform percentage of that total amount.

### 3.6.1 Emissions to Air

Traffic paints containing methyl chloroform are used for various road applications (lane lines, turn arrows, etc.). Because the primary mode of application is by spray equipment, it is assumed that no emission controls are used. Accordingly, it is assumed that 98 percent of the methyl chloroform used is emitted to the atmosphere as evaporative losses and the remaining 2 percent (unused amounts in containers, machinery cleaning residues) is disposed of in landfills. Uncertainties of ±2% and ±99% are assigned to the above assumptions, respectively, based on the relative confidence in the lack of emission controls used for spray application. The amount of methyl chloroform emissions to air can be calculated as follows:

| Amount of Methyl Chloroform Used in Paints Industry | Percent Emitted to Air During Use | | Amount Emitted to Air During Use |
|---|---|---|---|
| (5,000 kkg) | (0.99) | = | 4,950 kkg |

The uncertainty of the amount of methyl chloroform emitted to air is +106%, -99%, due to the uncertainty of +106%, -99%, for the amount of methyl chloroform used in the paints industry and the uncertainty of ±2% of the percent emitted to air.

### 3.6.2 Emissions to Water

Sampling programs have documented the presence of methyl chloroform in the wastewater effluent of paint manufacturing facilities. A recent study found methyl chloroform, at a mean concentration of 141 μg/liter, in approximately 50 percent of all paint facilities sampled (EPA, 1977e). The range of measured values for this study was 10 μg/liter to 930 μg/liter. Therefore, an uncertainty of ±50% was assigned to the mean concentration. The same study estimated the total amount of wastewater discharged to be 28,500,000 liters/yr. An uncertainty of ±25% was assigned to this estimate, as the survey did not contact all paint manufacturing facilities.

The amount of traffic paint produced in 1974 was estimated to be 95,000,000 liters, or 2.69 percent, of the total paint production in 1974

(EPA, 1979e). An uncertainty of ±10% was assigned to this estimate, due to the availability of information to document this estimate. It was assumed that the 1978 production level of traffic paints was equal to the 1974 figure, due to lack of data concerning 1978 production amounts.

Based on the above assumptions, the annual amount of methyl chloroform emissions to water can be calculated as follows:

| Amount of Wastewater Discharged by Paint Industry | Traffic Paint Percentage of Total Paint Production | Mean Amount of Methyl Chloroform Per Liter | = | Amount of Methyl Chloroform Discharged to Wastewater |
|---|---|---|---|---|
| (28,500,000 liters) | (0.0269) | ($1.41 \times 10^{-10}$ kkg) | = | $1.08 \times 10^{-4}$ kkg |

As shown above, the amount of methyl chloroform emissions to water are very small. Because traffic paints are solvent base paints, very little wastewater is generated from their formulation. Hence, the assumption that approximately 2.69 percent of the amount of wastewater discharged from the industry is due to traffic paint formulation processes is probably excessive. However, if the amount of wastewater was decreased, this would lower the amount of methyl chloroform discharged to wastewater, which is already at a minimum.

The uncertainty of the amount of methyl chloroform discharged to wastewater is ±57% because of the uncertainty of the amount of wastewater discharged by the paints industry (±25%), the uncertainty of the traffic paint percentage of total industrial production (±10%), and the uncertainty of the mean concentration of methyl chloroform in wastewater (±50%).

### 3.6.3 Emissions to Land

As stated earlier in Section 3.6.1, 2 percent (±99%) of the methyl chloroform used by the paint industry is emitted to land. The amount emitted to land can be calculated as follows:

| Amount of Methyl Chloroform Used by Paints Industry | Percent of Methyl Chloroform Emitted to Land | = | Amount of Methyl Chloroform Emitted to Land |
|---|---|---|---|
| (5,000 kkg) | (0.02) | = | 100 kkg |

The uncertainty of the amount of methyl chloroform emitted to land is +145%, -99%, due to the uncertainty of the amount of methyl chloroform used by the paint industry (+106%, -99%) and the uncertainty of the percent emitted to land (±99%).

### 3.6.4 Multimedia Environmental Losses

Figure 3.6-1 summarizes the multimedia emissions of methyl chloroform from the paints industry.

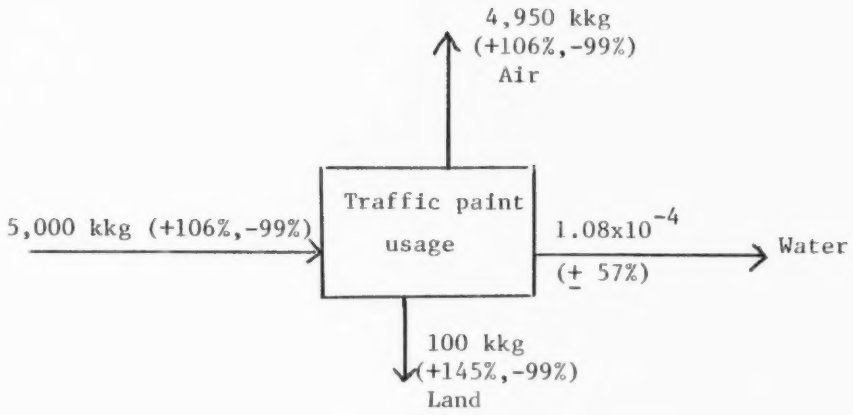

4,950 kkg
(+106%,-99%)
Air
5,000 kkg (+106%,-99%)
Traffic paint
usage
1.08x10^-4
(± 57%)
Water
100 kkg
(+145%,-99%)
Land

Figure 3.6-1 Multimedia Environmental Losses of Methyl Chloroform from Traffic Paints

## 3.7 INKS

Methyl chloroform is used in the ink industry as a grease cutter and as a cleaner for typewriter keys (MacGregor, H., 1979; Miller, W., 1979). Annual usage information was not available. However, methyl chloroform usage in the ink industry is assumed to be limited, as is the case for the paint industry. It is also worth noting that the metal cleaning aerosols industry and the adhesives industries comprise approximately 86 percent of the total United States methyl chloroform consumption and therefore only a small percentage of the methyl chloroform remains unaccountable. Because the ink industry uses only small quantities of methyl chloroform, it is assumed that 1 percent of the total production of methyl chloroform was used in 1978. This estimate has an uncertainty of ±75%, due to the lack of quantitative data. The uncertainty of the total production of methyl chloroform is +7%, -5%, due to its basis in International Trade Commission data. The amount of methyl chloroform used by the inks industry can be calculated as follows:

| Amount of Methyl Chloroform Produced in 1978 | Percent of Total Production Used by Ink Industry | | Amount of Methyl Chloroform Used by Ink Industry |
|---|---|---|---|
| | | = | |
| (284,000 kkg) | (0.01) | = | 2,840 kkg |

The uncertainty of the amount of methyl chloroform used by the ink industry is ±75%, due to the uncertainty of the total amount of methyl chloroform produced (+7%, -5%) and the uncertainty of the percent of total production used by the ink industry (±75%).

### 3.7.1 Emissions to Air

No emission controls were identified in the application of methyl chloroform as a grease cutter and a typewriter key cleaner. This seems reasonable because the cleaning of typewriter keys and machinery is done predominantly by hand application. It is assumed that 98 percent of the methyl chloroform used is emitted to the atmosphere as evaporative losses and the remaining 2 percent is disposed of in landfills due to quantities remaining in containers and industrial machinery cleaning residues. Uncertainties of ±2% and ±99% were assigned to these estimates, due to the confidence in the lack of emission controls. The amount of methyl chloroform released to air can be calculated as follows:

| Amount of Methyl Chloroform Used by Ink Industry | Percent Emitted to Air During Use | | Amount of Methyl Chloroform Emitted to Air |
|---|---|---|---|
| (2,840 kkg) | (0.98) | = | 2780 kkg |

The uncertainty of the amount emitted to the air is ±75%, due to the uncertainty of the amount used by the ink industry (±75%) and the uncertainty of the percent emitted to air (±2%).

### 3.7.2 Emissions to Water and Land

Data detailing emissions of methyl chloroform to water was not available. Based on the manner of its use, it was assumed that insignificant amounts were emitted to water.

As stated in Section 3.7.1, 2 percent (±99%) of the total amount of methyl chloroform used by the ink industry is emitted to land via landfill disposal. The amount emitted to land can be calculated as follows:

| Amount of Methyl Chloroform Used by Ink Industry | Percent Emitted to Land | | Amount of Methyl Chloroform Emitted to Land |
|---|---|---|---|
| (2,840 kkg) | (0.02) | = | 56.8 kkg |

The uncertainty of the amount of methyl chloroform emitted to land is +124%, -99%, due to the uncertainty of the amount used by the ink industry (±75%) and the uncertainty of the percent emitted to land (±99%).

### 3.7.3 Multimedia Environmental Losses

Figure 3.7-1 summarizes the multimedia emissions of methyl chloroform from the ink industry.

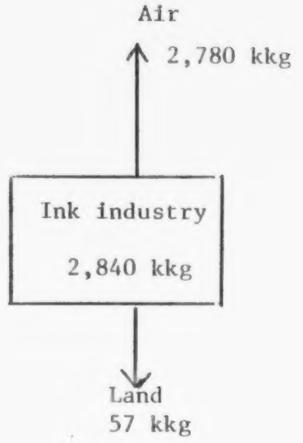

Air
2,780 kkg
Ink industry
2,840 kkg
Land
57 kkg

Figure 3.7-1 Multimedia Environmental Losses of Methyl Chloroform from the Ink Industry

## 3.8 Miscellaneous Minor Uses of Methyl Chloroform

Methyl chloroform is used in small quantities in a variety of industries as a solvent or degreaser.

Hydrophobic material-based catalyst preparations are formulated using organic compounds (such as methyl chloroform) as a solvent. In pharmaceuticals, methyl chloroform is used to extract active drug ingredients when non-polar solvents are required. Methyl chloroform provides the high gloss and weather-proofing properties required by the leather industry.

Other miscellaneous uses of emthyl chloroform are identified in Appendix D. Some of these products are included in other categories (for example: aerosol applied pesticides). Those products not included elsewhere represent approximately 2.5 percent (or 7,780 kkg) of the total methyl chloroform production. The environmental releases from these products were assumed to be similar to the losses from all other uses. Therefore, environmental emissions from other miscellaneous uses are the following:

| | | | |
|---|---|---|---|
| o | Destroyed | 145 kkg | ( 2%) |
| o | Air | 6730 kkg | (87%) |
| o | Water | 76 kkg | ( 1%) |
| o | Land | 829 kkg | (11%) |

### 3.8.1 Catalyst Preparation

Information on the use of methyl chloroform for the preparation of catalysts is not readily available. According to Bartholomew, organic chemicals, such as ethanol and chloroform, have sometimes been used as solvents in the preparation of hydrophobic material-based catalysts (Bartholomew, 1979). The quantity of methyl chloroform consumed in this category is not mentioned anywhere in the literature, and we suspect that this amount is very small ($<$0.01 percent) compared to other uses. An uncertainty of ±100% is assigned to this estimate, due to the lack of quantitative data. Furthermore, based on general application techniques of volatile solvents in catalyst preparation, 100 percent is assumed to be emitted to the air. The uncertainty of this estimate is ±10 percent, because the high volatility of methyl chloroform and the nature of its use ensures a high degree of volatilization.

Total consumption of methyl chloroform in catalyst preparations can be estimated as follows:

| Total 1978 Methyl Chloroform Production | Percent of Methyl Chloroform Used in Catalyst Production | = | Methyl Chloroform Used in Catalyst Production |
|---|---|---|---|
| (284,000 kkg) | (0.001) | = | 28.4 kkg |

The uncertainty of this value is ±100% due to the uncertainty for methyl chloroform production (+7%, -5%) and the uncertainty for the percent of total production consumed in catalysts (±100%). Since 100 percent is assumed to be emitted to the air, total air emissions from catalyst preparation is 28.4 kkg (±100%).

### 3.8.2 Film Cleaning

Methyl chloroform is used as a film cleaner because it is both nonflammable and an excellent degreaser (A. Knapp, Edwal Sci Products, 1979; M. Green, Polaroid, 1979; B. Klanderman, Eastman Kodak Co., 1979). However, methyl chloroform, because of its relatively high cost as compared with alcohol based cleaners, is limited to special applications, such as movie film cleaners.

Major users and distributors of film cleaners containing methyl chloroform were contacted (Edwal, 1979; Eastman-Kodak, 1979; Polaroid). As a result of these conversations, the amounts of methyl chloroform used by each were estimated at 15 kkg, 50 kkg, and 45 kkg, respectively. An uncertainty of ±50% was assigned to these estimates because they are based on verbal communications; and lack any quantitative data to validate the assumptions. During the course of these conversations, other users and distributors, besides the three contacted, could not be identified. Therefore, it was assumed that 50 percent of all the methyl chloroform used in the film cleaning industry was used by the three major users identified above. An uncertainty of ±30% was assigned to this estimate, since other industries which are dominated by a few companies have roughly similar market percentage ratios of 50:50 (split between large and small companies). Based on the above assumptions, the amount of methyl chloroform used by the film cleaning industry can be calculated as follows:

$$\frac{\text{Amount of Methyl Chloroform Used by Three Largest Companies}}{\text{Percentage of Total Methyl Chloroform Used by Three Largest Companies}} = \text{Amount of Methyl Chloroform Used by Film Cleaning Industry}$$

$$\frac{(15\text{ kkg} + 50\text{ kkg} + 45\text{ kkg})}{0.5} = 220\text{ kkg}$$

The uncertainty of the amount of methyl chloroform used by the film cleaning industry is ±58%, due to the uncertainty of the amount of methyl chloroform used by the three largest companies (±50%) and the uncertainty of the percentage of the total methyl chloroform used by the three largest companies (±30%).

### 3.8.2.1 Emissions to Air

Typically, cleaning film with methyl chloroform is done by hand application with a soft cloth (Knapp, A. W., Edwal Scientific Products, 1979). Because of this type of application, no emission control technology is assumed to be employed. As a film cleaner, methyl chloroform usually is packaged in small bottles (4 oz. to 16 oz.)(Knapp, A. W., 1979). Therefore, it was assumed that 99 percent of the methyl chloroform used is volatilized during use. An uncertainty of ±1% was assigned to this estimate, based on the confidence in the assumption that no emission control is used. The remaining 1 percent was assumed to be disposed of in landfills (accounting for unused amounts remaining in bottles). An uncertainty of ±98% was assigned to this estimate, also due to confidence in the assumption of no emission control. Accordingly, the amount of methyl chloroform emitted to the air can be calculated as follows:

| Amount of Methyl Chloroform Used by Film Cleaning Industry | Percent Emitted to Air During Use | = | Amount of Methyl Chloroform Emitted to Air from Film Cleaning |
|---|---|---|---|
| (220 kkg) | (0.99) | = | 218 kkg |

The uncertainty of the amount emitted to air is ±58%, due to the uncertainty of the amount used by the film cleaning industry (±58%) and the uncertainty of the percent emitted to air (±1%).

### 3.8.2.2 Emissions to Water and Land

Data detailing the amount of methyl chloroform discharged to wastewater from film cleaning was not available. It is assumed that wastewater discharges were insignificant, and are not calculated in this materials balance.

As stated in Section 3.8.2.1, 1 percent (±98%) of the total amount of methyl chloroform used by the film cleaning industry was disposed of in landfills. The amount of methyl chloroform emitted to the land can be calculated as follows:

| Amount of Methyl Chloroform Used by Film Cleaning Industry | Percent Emitted to Land During Use | | Amount of Methyl Chloroform Emitted to Land from Film Cleaning |
|---|---|---|---|
| (220 kkg) | (0.01) | = | 2.2 kkg |

The uncertainty of the amount emitted to land is +114%, -99%, due to the uncertainty of the amount used by the film cleaning industry (±58%) and the uncertainty of the percent emitted to land (±98%).

### 3.8.2.3 Multimedia Environmental Losses

Figure 3.8-1 summarizes the multimedia emissions of methyl chloroform from the film cleaning industry.

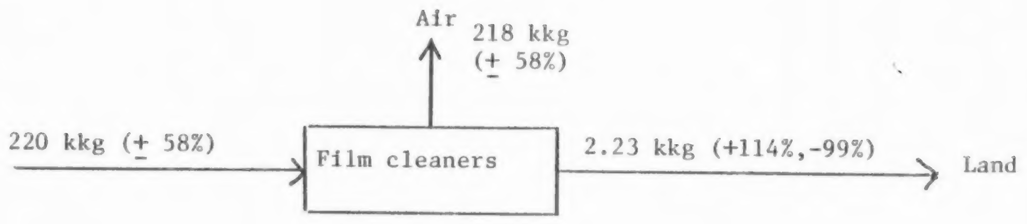

Air
218 kkg
(± 58%)
220 kkg (± 58%)
Film cleaners
2.23 kkg (+114%,-99%)
Land

Figure 3.8-1 Multimedia Environmental Losses of Methyl Chloroform from Film Cleaning

### 3.8.3 Pharmaceuticals

#### 3.8.3.1 Use of Methyl Chloroform

Since chlorinated solvents are used for extraction of active drug ingredients when non-polar solvents are required, the use of methyl chloroform in such applications was investigated. Contacts at the Bureau of Drugs indicated that methyl chloroform is not an active ingredient in any pharmaceutical, but that it may possibly be used in extraction procedures (Fehnel, P., 1979; Dr. Casola, 1979; Dr. Kukumian, 1979).

Methyl chloroform was found in the wastewater of several pharmaceutical companies during the Effluent Guidelines Survey of this industry (Neptune, D., 1978). Unfortunately, this data was not available for this study.

Several pharmaceutical companies were contacted regarding the use of methyl chloroform. Contacts at Upjohn, Bristol-Myers, Wyeth, Schering-Plough and Smith-Kline were not aware of any pharmaceutical procedures which use methyl chloroform, although they generally indicated that it could be used. Chlorinated solvents that were reportedly used in extraction procedures include chloroform and methylene chloride. (Street, E., 1979; Shrock, R., 1979; Wyeth, R+D Division, 1979; Henley, 1979; Bast, B., 1979).

Other possible uses of methyl chloroform in the pharmaceutical industries were also investigated. Based on industry contacts it does not seem likely that this solvent is used in drug capsule production (Henley, 1979), but may be used in small quantities for cleaning vessels and equipment (Street, E., 1979).

Although the pharmaceutical industries contacted are among the largest in the nation (these five companies are responsible for over 40 percent of all antibiotic sales) (Kirk-Ottomer, 1978), it is possible that some medicinal chemical processes do use methyl chloroform. The calculations which follow were made to determine methyl chloroform losses, assuming that a very small percentage of all chlorinated solvents used are methyl chloroform.

### 3.8.3.2 Multimedia Environmental Losses

Figure 3.8-2 shows a representative flow diagram of a process for production of medicinal compounds using chlorinated solvents.

Halogenated solvents are used in the extraction of active ingredients for medicinal chemicals and botanicals. Halogenated waste solvent generated in 1977 was estimated at 3,800 kkg and 70 kkg for these two processes, respectively, and were projected to increase at a rate of 7 percent per year (EPA, 1976). Based on conversations with pharmaceutical houses it seems reasonable to assume that not more than 5 percent of chlorinated waste solvent is methyl chloroform. Based on these assumptions we estimate the quantity of methyl chloroform in waste solvent as follows:

| | | | |
|---|---|---|---|
| Quantity of Total Halogenated Waste Solvent Generated | Growth Rate | = | Quantity of Halogenated Waste Solvent Generated in 1978 |
| (3800 kkg + 70 kkg) | (1.07) | = | 4140 kkg |
| Quantity of Halogenated Waste Solvent Generated in 1978 | Percent which is Methyl Chloroform | = | Methyl Chloroform Waste Solvent Generated in 1978 |
| (4140 kkg) | (0.05) | = | 207 kkg |

This estimate is not considered more accurate than +25 and -100%. An uncertainty of -100% accounts for the possibility (although unlikely) that no methyl chloroform is used by the pharmaceutical industry.

JRB assumes that all waste solvent was unreclaimed solvent from solvent recovery systems. These systems operate, on an average, at 95 percent efficiency (±4%). Then, the total methyl chloroform used by the industry is estimated as follows:

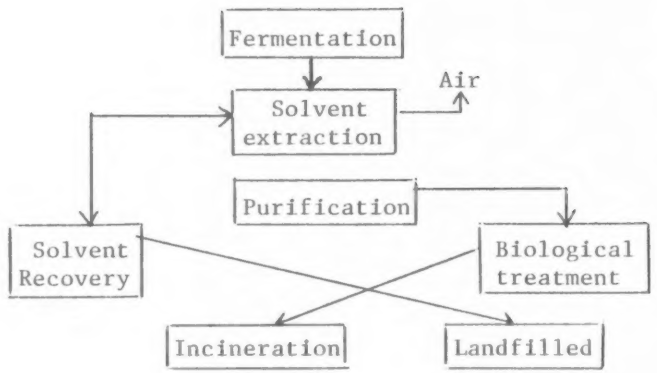

Fermentation
Solvent extraction
Air
Purification
Solvent Recovery
Biological treatment
Incineration
Landfilled

Figure 3.8-2 Typical Process for Extraction of Medicinal Chemicals

| Quantity of Waste Generated | ÷ | Percent of Solvent which is Waste Solvent | = | Total Methyl Solvent Chloroform Used |
|---|---|---|---|---|

$$\frac{(207\ \text{kkg})}{0.05} = 4140\ \text{kkg}$$

It is also assumed that 3 percent (±50%) of the total solvent is emitted to air during production. This low percent release assumes that enclosed vessels are regularly used for extractions.

| Total Methyl Chloroform Used in Pharmaceuticals | Percent Emitted to Air | = | Quantity Emitted to Air |
|---|---|---|---|
| (4140 kkg) | (0.03) | = | 124 kkg |

This estimate is not considered more accurate than +98% and -100%. The range accounts for uncertainties related to the qquantity of methyl chloroform used (4140, +84%, -100%) and the percent released to air (0.03, ±50%).

Based on a survey conducted by the EPA, about 50 percent of large pharmaceutical companies have on-site incineration and many other companies contract waste to be incinerated off site. Only small companies and R&D installations landfill waste solvent (EPA, 1976). We assume 90 percent (±5%) of the waste is incinerated at 95 percent efficiency (±4%) and 10 percent (±50%) is landfilled.

| Methyl Chloroform Solvent | Percent Incinerated | Efficiency | = | Quantity Waste Incinerated (Destroyed) |
|---|---|---|---|---|
| (207 kkg) | (0.9) | (0.95) | = | 177 kkg |

| Methyl Chloroform Waste Solvent | Percent Incinerated | 1-Efficiency | = | Quantity Emitted to Air |
|---|---|---|---|---|
| (207 kkg) | (0.9) | (1-0.95) | = | 9.32 kkg |

| Methyl Chloroform Waste Solvent | Percent Landfilled | = | Quantity Landfilled |
|---|---|---|---|
| (207 kkg) | (0.1) | = | 20.7 kkg |

Uncertainties for these estimates are: +84%, -100% for the quantity incinerated; +116%, -100% for releases to air from incineration and +98%, -100% for the quantity landfilled.

Figure 3.8-3 shows multimedia losses of methyl chloroform from production of medicinal chemicals, based on assumptions discussed above.

Based on these estimates, 41 percent of the methyl chloroform losses from the pharmaceutical industry is emitted to air, 53 percent is incinerated and the remaining 6 percent is landfilled.

Use of methyl chloroform as a solvent in pharmaceutical processes could be confirmed by reviewing new drug applications on record with the Bureau of Drugs. However, clearance to review these records could not be obtained for this study.

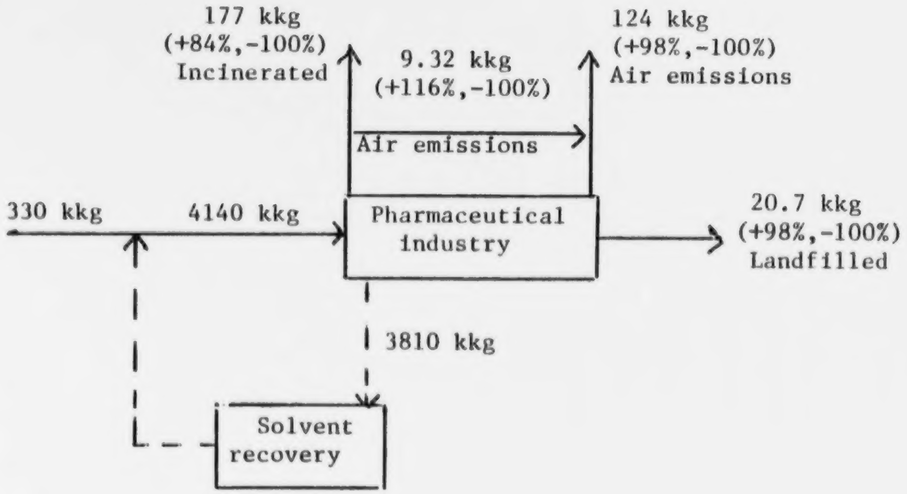

177 kkg
(+84%,-100%)
Incinerated
9.32 kkg
(+116%,-100%)
124 kkg
(+98%,-100%)
Air emissions
Air emissions
330 kkg
4140 kkg
Pharmaceutical industry
20.7 kkg
(+98%,-100%)
Landfilled
3810 kkg
Solvent recovery

Figure 3.8-3 Multimedia Environmental Losses of Methyl Chloroform from Pharmaceutical Processes

### 3.8.4 Leather Tanning and Finishing

Investigations were conducted to determine the amounts of use and the magnitude of multimedia emissions of methyl chloroform from its use in the leather tanning and finishing industry. Quantitative data could not be obtained detailing the amount of methyl chloroform used by the industry. However, it was determined that it is used by various segments of the industry, and that air and water emissions occur. Figure 3.8-4 details a typical complete chrome tannery.

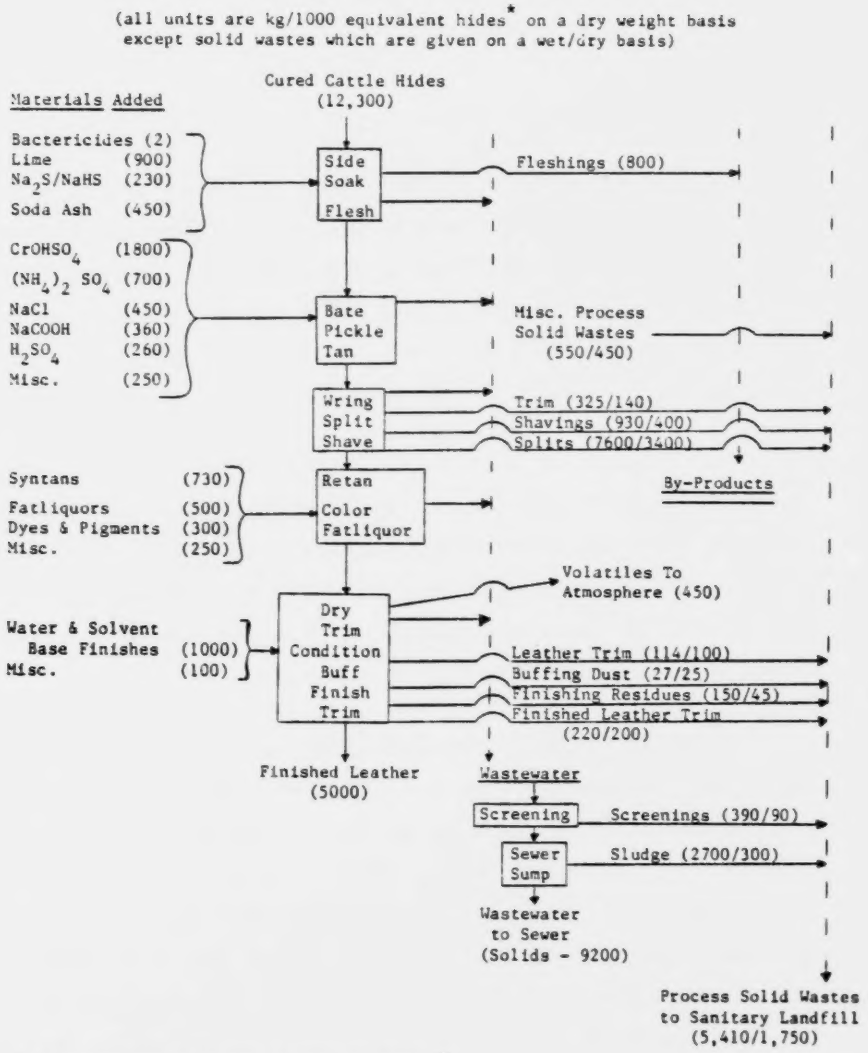
#### 3.8.4.1 Emissions to Air

It was determined that solvents are used in the tanning finishing process, although their use is being curtailed due to handling difficulties and their inherent fire hazard (EPA, 1979b). During this process, a water or solvent based finish is applied to give the leather the required pattern gloss or waterproof qualities. Methyl chloroform is used in the finishing process as a carrier for water and stain repellant (EPA, 1979b).

Application of the finish is typically done in a spray booth, which is equipped with an exhaust air water wash system to remove fumes and particulates from the spray booth working environment (SCS Engineers, Inc., 1976). The particulates are collected by the wash system, while the fumes are vented to the atomosphere. A flow diagram of a typical leather finishing process is presented in Figure 3.8-5.

Volatile organic compound (VOC) air emissions from these operations have been estimated to be 0.45 kkg per 1000 equivalent hides, where an equivalent hide has an area of 40 ft$^2$ (Department of Commerce, 1976) and a weight of 0.023 kkg (Rapp, 1980). An uncertainty of ±25% is assigned to the amount of volatile organic compound emissions, due to the volatility of methyl chloroform and VOC's and their use as a carrier agent. No significant chemical absorption of methyl chloroform (or other VOC's) by the finish occurs. There is no uncertainty relative to the area of an equivalent hide, as this is an established unit of measurement. An uncertainty of ±20% is assigned to the stated weight of an equivalent hide, due to the range of the verbal estimate obtained (0.018 kkg to 0.028 kkg).

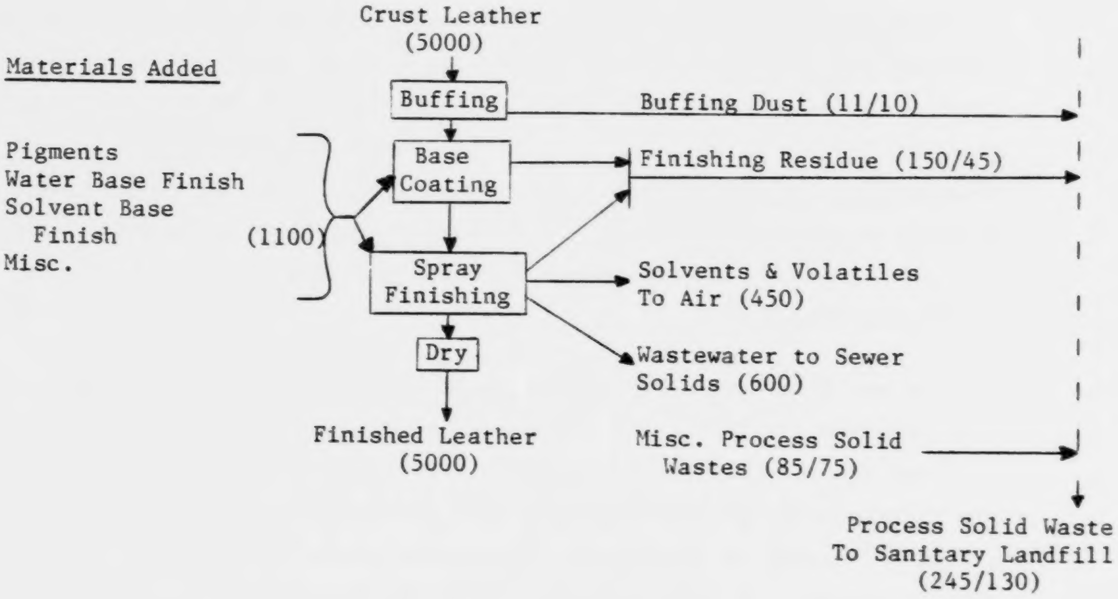
Figure 3.8-4 -- Flow Diagram for the Chrome Tanning Process


(all units are kg/1000 equivalent hides* on a dry weight basis except solid wastes which are given on a wet/dry basis)
Materials Added
Cured Cattle Hides (12,300)
Bactericides (2)
Lime (900)
$Na_2S$/NaHS (230)
Soda Ash (450)
Side Soak Flesh
Fleshings (800)
$CrOHSO_4$ (1800)
$(NH_4)_2SO_4$ (700)
NaCl (450)
NaCOOH (360)
$H_2SO_4$ (260)
Misc. (250)
Bate Pickle Tan
Misc. Process Solid Wastes (550/450)
Wring Split Shave
Trim (325/140)
Shavings (930/400)
Splits (7600/3400)
By-Products
Syntans (730)
Fatliquors (500)
Dyes & Pigments (300)
Misc. (250)
Retan Color Fatliquor
Volatiles To Atmosphere (450)
Water & Solvent Base Finishes (1000)
Misc. (100)
Dry Trim Condition Buff Finish Trim
Leather Trim (114/100)
Buffing Dust (27/25)
Finishing Residues (150/45)
Finished Leather Trim (220/200)
Finished Leather (5000)
Wastewater
Screening
Screenings (390/90)
Sewer Sump
Sludge (2700/300)
Wastewater to Sewer (Solids - 9200)
Process Solid Wastes to Sanitary Landfill (5,410/1,750)

* An equivalent hide has an area of 40 ft.$^2$

Figure 3.8-5 -- Flow Diagram for a Typical Leather Finishing Process

(All units are kg/1000 equivalent hides on a dry weight basis except solid wastes which are given on a wet/dry basis)


Crust Leather
(5000)
Materials Added
Buffing
Buffing Dust (11/10)
Pigments
Water Base Finish
Solvent Base
Finish
Misc.
(1100)
Base
Coating
Finishing Residue (150/45)
Spray
Finishing
Solvents & Volatiles
To Air (450)
Dry
Wastewater to Sewer
Solids (600)
Finished Leather
(5000)
Misc. Process Solid
Wastes (85/75)
Process Solid Waste
To Sanitary Landfill
(245/130)

* An equivalent hide has an area of 40 ft.$^2$

Data could not be found which detailed the constituents of the VOC emissions occurring from leather tanning and finishing processes. Eighteen volatile organic compounds (VOC's) have been identified in leather tanning facility wastewater effluents (EPA, 1979b). Of these 18, benzene, dichloromethane, ethylbenzene, toulene, and trichloromethane appeared in 17, 17, 23, 22, and 11 of the 24 facilities analyzed, respectively. Because methyl chloroform appeared in only 6 of the facilities studied, and due to the lack of other pertinent information, it is assumed that methyl chloroform constitutes only 1 percent of the total volatile organic compound (VOC) emissions resulting from leather finishing. An uncertainty of ±95% is assumed for this estimate due to the lack of corroborating information.

It was determined that an estimated 23,000,000 equivalent hides were processed in 1976 (EPA, 1979b). The industry experienced a decline in since the mid-1960's, and began to increase in 1974 (EPA, 1979b). Therefore, it was assumed that the 1978 level of production will remain at the 1976 level of 23,000,000 equivalent hides. An uncertainty of ±10% is assigned to this estimate due to the error inherent in production estimates, although the estimate is based on substantial data.

Based on the above assumptions, the amount of methyl chloroform air emissions from the finishing process can be calculated as follows:

| Amount VOC per Equivalent Hides | | Percent Methyl Chloroform in VOC | | Amount of Equivalent Hides Processed 1978 | | Amount of Methyl Chloroform Volatilized from Finishing Process |
|---|---|---|---|---|---|---|
| .00045 kkg/hide | x | 0.1 | x | 23,000,000 hides | = | 104 kkg |

The uncertainty of the amount of methyl chloroform volatilized from the finishing process is ±99%, due to the uncertainty of the amount of VOC per hide (±25%), the uncertainty of the percent of methyl chloroform in the VOC (±95%), and the uncertainty of the amount of equivalent hides processed in 1978 (±10%).

### 3.8.4.2 Emissions to Water

Seven subcategories have been developed which depict the manufacturing process of the leather industry from the handling of raw materials through the finished product (EPA, 1979b). Methyl chloroform was identified in three of these subcatogories during a wastewater sampling and analysis program involving 22 of the estimated 188 leather tanning and finishing plants in the United States.

Subcateogry 1, "Hair Pulp/Chrome Tan/Retan-Wet Finish," consists of facilities which primarily process raw or cured cattle or cattle-like hides into finished leather products by chemically dissolving the hair, tanning with chrome,and retanning and wet finishing. Methyl chloroform has been detected in the wastewater effluent from 1 out of 3 such facilities tested, at a mean concentration of "present;" that is, detectable but below the quantifiable level. Methyl choloroform is presumably used as a solvent and degreasing agent, as a solvent carrier for water and stain repellant compounds, as a solvent for organics (oil, greases, waxes, fats, tars), as a flammability retardant, and to add solvent properties.

Subcategory 2, "Hair Save, Chrome Tan, Retan-Wet Finish," consists of facilities which employ the same processes as Subcategory 1 facilities, but which chemically loosen and mechanically remove the tar. Methyl chloroform has also been detected in the wastewater effluent of 1 of 2 facilities tested, at a mean concentration of 10 $\mu$g/liter. Methyl chloroform is presumably used in the same applications stated earlier for Subcategory 1 facilities.

Subcategory 6, "Through-the-Blue," consists of facilities which process raw or cured cattle or cattle-like hides into the blue tanned state only by chemically dissolving the hair and tanning with chrome, with no retanning or wet finishing. As with Subcategory 1, methyl chloroform was detected at a mean concentration of "present" in the wastewater effluent of only facility tested. Methyl chloroform is presumably used in the same applications as for Subcategory 1. However, because there is no retan or wet finish, it is not used as a solvent carrier for water and stain repellants.

A number of assumptions were made to calculate water emissions from Subcategories 1, 2, and 6. Water consumptions for Subcatoegories 1, 2, and 6 were determined to be 38,000, 46,000, and 23,000 liters/kkg, respectively (EPA, 1979b). Data was not available concerning the number of hides processed per subcategory, which would have enabled calculation of methyl chloroform emissions from each subcategory. Therefore, an average of the three flow rates was calculated (35,600 liters/kkg of equivalent hide). An uncertainty of ±35% was estimated for this average flow rate, as a result of the incompleteness of the survey (22 out of 188 tanneries sampled). Also, approximately 50 percent of the plants in these three subcategories reported flows below the average mean.

As stated earlier, the amount of methyl chloroform in the effluent of subcategories 1, 2, and 6 ranged from "present" to 10μg/liter. Accordingly, it is estimated that the amount of methyl chloroform in the effluent is 10 μg/liter, assuming worst case. An uncertainty of ±95% is assigned to this estimate, based on the restricted number of tanneries sampled and the number of samples taken.

The weight of a liter of methyl chloroform was calculated. Based on a density of 1.3390 (Weast, 1972), it was determined that one liter of methyl chloroform had a mass of 0.00134 kkg. A low uncertainty of ±5% was assigned to this calculation, due to the empirical nature of densities.

As stated earlier in Section 3.8.4.1, one equivalent hide has a mass of 0.23 kkg, ±20%.

Based on the above assumptions, the amount of methyl chloroform discharged to water can be calculated as follows:

| Number of Equivalent Hides Processed per Year | Mass of an Equivalent Hide | Amount of $H_2O$ Used per kkg of Equivalent Hide | Amount of Methyl Chloroform per Liter of Water | = | Amount of Methyl Chloroform Discharged to Water |
|---|---|---|---|---|---|
| (23,000,000) hides | (0.23) kkg/hide | (35,600) liters/kkg | (1 x $10^{-11}$) kkg/liter | = | 1.88 kkg |

The uncertainty of the amount of methyl chloroform discharged to wastewater is ±42%, due to the uncertainties, stated earlier, of each factor in the equation.

### 3.8.4.3 Multimedia Environmental Losses

Figure 3.8-6 summarizes the multimedia emissions of methyl chloroform from the leather tanning and finishing.

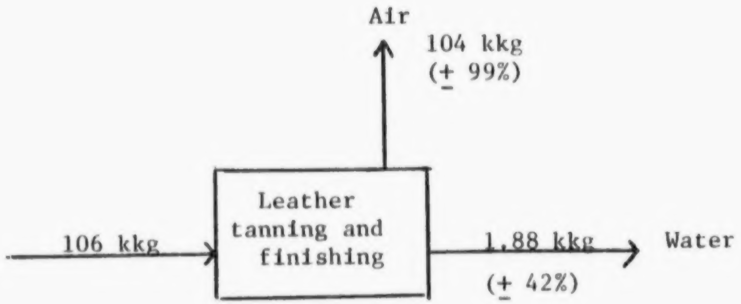

Air
104 kkg
(± 99%)
106 kkg
Leather tanning and finishing
1.88 kkg
(± 42%)
Water

Figure 3.8-6 Multimedia Environmental Losses of Methyl Chloroform in the Tanning Industry

## 3.9 EXPORTS

### 3.9.1 Export of Methyl Chloroform - 1978

The total U.S. export of methyl chloroform in 1978 was 18,000 kkg (± 10%) or 6.4 percent of the total production (Schedule B, U.S. ITC, 1979). Table 3.9-1 shows the distribution of exports to various countries and the percentage of total methyl chloroform exports imported by each country.

TABLE 3.9-1 - U.S. Export of Methyl Chloroform

| Country | Methyl Chloroform Exported kkg | Percent of Total Export |
|---|---|---|
| Algeria | 7 | 4 |
| Argentina | 192 | 1 |
| Australia | 4,983 | 28 |
| Bahamas | 34 | 1 |
| Barbados | 5 | 1 |
| Belgium | 10 | 1 |
| Bolivia | 1 | 1 |
| Brazil | 3,570 | 20 |
| Canada | 439 | 2 |
| Chile | 22 | 1 |
| China | 20 | 1 |
| Columbia | 45 | 1 |
| Costa Rica | 3 | 1 |
| Dominican Republic | 20 | 1 |
| Ecuador | 3 | 1 |
| France | 304 | 2 |
| Germany-West | 503 | 3 |
| Guatamala | 11 | 1 |
| Haiti | 34 | 1 |
| Honduras | 1 | 1 |
| Hong Kong | 0.5 | 1 |
| Indonesia | 3 | 1 |
| Iran | 10 | 1 |
| Israel | 42 | 1 |
| Jamaica | 10 | 1 |
| Japan | 1,810 | 10 |
| Jordan | 9 | 1 |
| Korea | 29 | 1 |
| Lebanon | 0.4 | 1 |
| Mexico | 452 | 3 |

TABLE 3.9-1 - U.S. Export of Methyl Chloroform (cont.)

| Country | Methyl Chloroform Exported kkg | Percent of Total Export |
|---|---|---|
| Netherlands | 1 | 1 |
| Nigeria | 0.4 | 1 |
| Philippines | 11 | 1 |
| Rep. S. Africa | 14 | 1 |
| Salvadore | 5 | 1 |
| Singapore | 4,895 | 27 |
| South Arabia | 4 | 1 |
| Spain | 0.3 | 1 |
| Sudan | 1 | 1 |
| Surinam | 0.2 | 1 |
| Switzerland | 1 | 1 |
| Trinidad | 9 | 1 |
| T. Pac I | 11 | 1 |
| United Kingdom | 300 | 2 |
| Uruguay | 3 | 1 |
| Venezuela | 193 | 1 |
| Zaire | 1 | 1 |

Source: U.S. ITC, 1979

Eighty-five percent of the 1978 exports went to Japan, Brazil, Australia, and Singapore; all other countries imported 3 percent or less.

### 3.9.2 Method of Export

Methyl chloroform is exported to approximately 50 countries in annual quantities varying from 1 - 20,000 barrels (1 kkg = 4 barrels). All importing countries require marine transport except for Mexico and Canada where road or rail transport is possible. Mexico and Canada will not be considered separate from the remaining importing countries, because their combined annual import is only 5 percent of the total U.S. export of methyl chloroform (see Table 3.9-1).

Methyl chloroform is transported abroad in 54 gallon barrels via container ships.

Due to its volatile nature and the absence of vapor recovery systems at marine terminals, significant methyl chloroform losses could occur during the loading and offloading of cargo unless the cargo is packaged in a closed container such as a barrel.

For example, one percent of the cargo transferred during the loading of crude oil is lost via evaporation with even greater losses probable for volatile methyl chloroform (DOE, 1978). The quantities exported are quite small in comparison to the cargo capacity of a relatively small tanker. An 18,000 deadweight ton tanker has a cargo capacity of 120,000 barrels with an individual tank typically holding 7,000 barrels. Therefore, shipments would require containers on the order of a barrel as opposed to the tanks of a tanker. The filling of barrels with methyl chloroform is assumed to take place at the production site. Losses of methyl chloroform from this operation has been included in evaporation emissions at the production site. Emissions of methyl chloroform do not usually occur during the transport of a sealed barrel.

### 3.9.3 Trends in the Export of Methyl Chloroform

U.S. exports of methyl chloroform in 1968 and from 1973-1978 are presented in Table 3.9-2 (EPA, 1979a). Export amounts for the years 1973-1975 reflect an increased usage of methyl chloroform abroad. A decrease in exports in the subsequent years can be attributed to increased foreign production capacity. Therefore, future export quantities of methyl chloroform should remain steady, as exhibited by the 1976-78 export quantities. It is not likely that methyl chloroform exports will return to the large quantities of 1973-75. Thus, we expect that the export of methyl chloroform should remain on the order of 20,000 kkg during the next few years.

Table 3.9-2 -- U.S. Exports of Methyl Chloroform

| Year | Exports (kkg) |
|---|---|
| 1968 | 18,000 |
| 1973 | 35,000 |
| 1974 | 37,000 |
| 1975 | 21,000 |
| 1976 | 14,000 |
| 1977 | N/A |
| 1978 | 18,000 |

Source: EPA, 1979a.
Bureau of Census, 1979.

## 4.0 DISPOSAL AND DESTRUCTION OF END PRODUCTS

### 4.1 Contamination of End Products

The presence of methyl chloroform in other products as an impurity has been carefully analyzed since little information exists on this subject. According to a typical analysis of vinylidene chloride monomer, methyl chloroform has been reported at 150 ppm by weight (Mark, Gaylord, 1971). Unfortunately, the source of this figure is not discussed in the report. The same report also details a typical analysis of vinyl chloride monomer. The results of the analysis does not identify any traces of methyl chloroform among the reported impurities. Methyl chloroform was not identified as a contaminant of other chemical products although several references on this subject were consulted. (EPA, 1979a; TRW, 1975; EPA, 1977; EPA 1972)

### 4.1.1 Emission of Methyl Chloroform as a Contaminant of Vinylidene Chloride Products

The quantity of vinylidene chloride monomer produced in 1978 was estimated at 77,000 kkg (SRI, 1975). Based on this assumption, the amount of methyl chloroform introduced to the environment as an impurity of vinylidene chloride monomer can be calculated by multiplying the following factors:

1) the quantity of vinylidene chloride produced in 1978
2) the contaminated level of methyl chloroform in vinylidene chloride monomer

Therefore:

$$(77{,}000 \text{ kkg})\ (150 \times 10^{-6}) = 12 \text{ kkg}.$$

This quantity is eventually destroyed during the consumption of vinylidene chloride monomer in the production of its polymer and other end-products. Therefore, the net release of methyl chloroform to the environment from the production and use of vinylidene chloride monomer is neither measurable nor quantifiable ($\sim$0 kkg).

## 4.2 Summary of Disposal and Destruction of End Products

This chapter summarizes the information pertaining to the quantities of methyl chloroform landfilled and the quantities destroyed. Incineration was the only significant method used to destroy methyl chloroform wastes in 1978. Biological degradation undoubtedly plays a very minor role.

Table 4.2-1 shows that 76 percent of the methyl chloroform produced is lost directly to air and water within one year. Only about 2 percent is destroyed by incineration. Of the methyl chloroform produced, 9.2 percent was landfilled in 1978 as waste solvent in sludge or still bottoms or as residue in cans. Because of the volatile nature of methyl chloroform, improperly landfilled methyl chloroform wastes would be readily evaporated. Table 4.2-1 shows estimates for the percentage of landfilled wastes that could typically be expected to be lost by evaporation within one year. The losses depend upon the type of container used and their resistance to crushing or impaction. The rationale for our estimates of percent evaporation is discussed in Table 4.2-1. By multiplying the percent evaporation from each end use times the quantity landfilled from each end use, and taking the average of the total emissions, it was determined that 31 percent of the methyl chloroform landfilled will evaporate per year (see Table 4.2-1).

In order to estimate the cumulative load of methyl chloroform in landfills since production startup in 1951, emission controls, waste disposal practices and quantities of methyl chloroform used for each particular end use are required. Acquisition of this data was not within the scope of this study. The cumulative load was estimated for the 5 year period from 1974-1978 by assuming that waste disposal practices (total of 9.2 percent landfilled annually) and the percent of methyl chloroform used for each particular end use were constatn over this five year period. We estimated an annual release rate from landfills of 29 percent. Table 4.2-2 shows quantities landfilled and cumulative load in landfills over the 5 year period (1974 through 1978). The quantity of methyl chloroform accumulated in landfills is 49,700 kkg.

TABLE 4.2-1 -- Disposal and Destruction of End Products

| Process | Air Plus Water | Lost By Incineration | Landfilled (kkg) | % Released from Landfill in One Year | Amount in Landfill (kkg) | Rationale for Estimate of Percent Release |
|---|---|---|---|---|---|---|
| Cold Cleaning | 37,100 | 870 | 7,600 | 25 | 5,700 | It was assumed that 75% of the wa t is adequately containerized and will not leach within 1 year period. |
| Open Top Vapor Degreasing | 79,100 | 2,190 | 10,500 | 25 | 7,880 | |
| Conveyorized Vapor Degreasing | 35,200 | 905 | 3,270 | 25 | 2,450 | |
| Conveyorized Non-Boiling Degreasers | 9,490 | 236 | 863 | 25 | 647 | |
| Adhesives | 17,700 | 57 | 919 | 25 | 689 | |
| Aerosols | 18,100 | - | 1,890 | 75 | 473 | Methyl chloroform will leach when containers are crushed and compacted. Slow release due to improperly tightened cans. |
| Paints | 4,950 | - | 100 | 75 | 25 | |
| Inks | 2,780 | - | 57 | 100 | 0 | Small containers are probably not tightened sufficiently to prevent losses. |
| Drain Cleaners | 289 | - | 303 | 10 | 273 | Lost from the sludge only when the septic tank is pumped. |
| | 908* | | | | | |
| Textiles | 2,920 | - | 18 | 25 | 14 | See metal cleaning |
| Film Cleaners | 218 | - | 2 | 100 | 0 | Small containers are probably not tightened sufficiently to prevent losses. |
| Pharmaceuticals | 124 | 177 | 21 | 25 | 16 | It was assumed that 75% of the waste is properly containerized and will not leach within 1 year period. |
| Miscellaneous | 6,940 | 145 | 829 | - | 622 | See metal cleaning |
| TOTAL | 215,800 | 4,580 | 26,400 | | 18,800 | |
| PERCENT TOTAL | | 1.6 | 9.3 | | 71% (Percent of Total Landfilled) | |

* - Groundwater Discharge

SUMMARY OF METHYL CHLOROFORM LANDFILLED
TABLE 4.2-2 OVER 5 YEAR PERIOD (kkg)

| Year | U.S. Production | Quantity to Landfill (1) | Quantity Released from Landfill | Quantity in Landfill (cumulative) |
|---|---|---|---|---|
| 1974 | 268,000 | 24,700 | 7,200 | 17,500 |
| 1975 | 208,000 | 19,100 | 5,500 | 26,000 |
| 1976 | 261,000 | 24,000 | 7,000 | 35,500 |
| 1977 | 287,000 | 26,400 | 7,700 | 43,900 |
| 1978 | 284,000 | 26,100 | 7,600 | 49,700 |

(1) Assumes 9.2% landfilled annually

Although not an end product, stockpiles represent a significant quantity of methyl chloroform not released to the environment. Using the data found in Section 2.7.1, we estimate the quantity of methyl chloroform in stockpiles is approximately 120,000 kkg. If the three producers stopped production, at the present rate of methyl chloroform use, existing stockpiles would be consumed within 5 months.

## 5.0 SUMMARY OF ENVIRONMENTAL RELEASES OF METHYL CHLOROFORM

The discussion of this section will help pinpointing locations where large emissions of methyl chloroform can potentially occur.

The largest quantity of methyl chloroform emitted to the environment is due to the use of this chemical as a solvent in cold cleaning and vapor degreasing. Cold cleaning and vapor degreasing establishments are dispersed throughout the United States, but are more heavily concentrated in the northeast.

Other potential "hot spots" where large emission of methyl chloroform can occur are industrial users of solvent based adhesives and the production sites of this chemical. As previously discussed, the location of methyl chloroform production facilities are situated in the Gulf Coast of the United States, particularly in Freeport, Texas and in Geismar and Lake Charles, Louisiana. These locations are probably most heavily exposed to methyl chloroform.

## 6.0 SUMMARY OF UNCERTAINTIES

Table 6.0-1 lists the estimates for environmental releases of methyl chloroform by process and by media of release. The uncertainty of each number is included in the table to give the reader easy access to the uncertainty of each estimate. The rationale for assigning a specific uncertainty of each number is discussed in detail in Chapters 2 and 3. Our recommendations for "fine tuning" the material balance to reduce the uncertainty of these estimates is discussed in Chapter 7.

The uncertainties were calculated by taking the square root of the sum-of-the-squares of individual uncertainties unless otherwise specified.

An example from the text is presented below:

Section 2.2.2.2 - Air Emissions from Intermediate Storage

Air Emissions = 179 x $10^3$ kkg (+6%, -7%) x 0.05 kkg/$10^3$ kkg
(±25%) x {4% x 1%}(±24%) x 1-85% (±5%) * =
0.000537 kkg (±49%)

Upper Bound -

$$\sqrt{(.06)^2 + (.25)^2 + (.25)^2 + (.33)^2} \quad = .49 \text{ or } 49\%$$

Lower Bound -

$$\sqrt{(.07)^2 + (.25)^2 + (.25)^2 + (.33)^2} \quad = .49 \text{ or } 49\%$$

*Note: 1 - 85% (±5%) is equivalent to 15% (±33%)

TABLE 6-1

SUMMARY OF UNCERTAINTIES

| Process/Operation | Waste | Quantity (kkg) | Uncertainty (%) |
|---|---|---|---|
| Total U.S. Production | - | 284,000 | +7/-5 |
| Production - Vinyl Chloride | Total methyl chloroform produced | 179,000 | +6/-7 |
| | o Direct emissisons to air | 6.62 | ±50 |
| | o Emissions to air from air pollution controls | 74.1 | +171/-57 |
| | o Quantity landfilled | $3.58 \times 10^{-5}$ | +103/-100 |
| | o Quantity emitted to air from incineration | $1.79 \times 10^{-6}$ | +131/-100 |
| | o Quantity retained in water | 0.133 | ±35 |
| | o Quantity volatilized from water | 13.9 | +107/-62 |
| Production - Ethane | Total methyl chloroform produced | 25,500 | +10/-2 |
| | o Direct emissions to air | 2.89 | +60/-59 |
| | o Emissions to air from air pollution controls | 6.31 | +61/-52 |
| | o Quantity landfilled | 0.00383 | +112/-100 |
| | o Quantity emitted to air from incineration | 0.000191 | +138/-100 |
| | o Quantity retained in water | 0.430 | ±41 |
| | o Quantity volatilized from water | 4.48 | +109/-66 |

| Process/Operation | Waste | Quantity (kkg) | Uncertainty (%) |
|---|---|---|---|
| Production - Vinylidene **Chloride** | Total methyl chloroform produced | 79,500 | +0/-14 |
| | o Direct emissions to air | 2.94 | +54/-56 |
| | o Emission to air from air pollution controls | 48.5 | +365/-99 |
| | o Quantity landfilled | ~0 | - |
| | o Quantity emitted to air from incineration | 3.98 | +80/-81 |
| | o Quantity retained in water | 0.115 | ±31 |
| | o Quantity volatilized from water | 12.0 | +106/-60 |
| Metal Cleaning | Total methyl chloroform used in metal cleaning | 187,700 | +11/-2 |
| | Total in vapor degreasing | 131,400 | +11/-21 |
| | Total in cold cleaning | 56,300 | +39/-2 |
| | Total used for non-conveyorized cold cleaning | 45,700 | +39/-2 |
| | o Releases to water | 8,530 | +43/-33 |
| | o Releases to land | 7,600 | +46/-29 |
| | o Quantity incinerated | 623 | +77/-85 |
| | o Air emissions | 28,600 | +58/-29 |
| | Total used for open top vapor degreasing | 91,700 | +35/-39 |
| | o Releases to water | 8,470 | +20/-21 |
| | o Releases to land | 10,500 | +38/-74 |
| | o Quantity incinerated | 1,580 | +37/-76 |

| Process/Operation | Waste | Quantity (kkg) | Uncertainty (%) |
|---|---|---|---|
| Metal Cleaning (cont.) | o Air emissions | 70,600 | +42/-41 |
| | Total used for conveyorized vapor degreasers | 39,300 | +35/-39 |
| | o Releases to water | 2,000 | +60/-61 |
| | o Releases to land | 3,270 | +69/-93 |
| | o Quantity incinerated | 619 | +68/-95 |
| | o Air emissions | 33,200 | +35/-39 |
| | Total used for conveyorized non-boiling degreasers | 10,600 | +34/-32 |
| | o Releases to water | 546 | ±35 |
| | o Releases to land | 863 | +52/-47 |
| | o Quantity incinerated | 159 | +51/-52 |
| | o Air emissions | 8,940 | +47/-46 |
| Aerosols | Total methyl chloroform in adhesive products | 20,000 | ±20 |
| | Methyl chloroform in household products | 3,000 | ±36 |
| | o Emissions to air during production | 75.0 | ±41 |
| | o Releases to air from use | 2,640 | ±41 |
| | o Quantity landfilled | 293 | ±99 |
| | Total methyl chlorform used in aerosol products | 500 | +56/-44 |
| | o Emissions to air during production | 12.5 | ±41 |
| | o Emissions to air from end-use | 439 | ±41 |
| | o Quantity landfilled | 48.8 | ±99 |

| Process/Operation | Waste | Quantity (kkg) | Uncertainty (%) |
|---|---|---|---|
| Aerosols (cont.) | Total methyl chloroform used in coating and finishing products | 1,500 | ±36 |
| | o Emissions to air during production | 37.5 | ±41 |
| | o Emissions to air from end-use | 1,320 | ±41 |
| | o Quantity landfilled | 146 | ±99 |
| | Total methyl chloroform in personal care and pesticide products | 15,000 | ±36 |
| | o Emission to air during formulation | 375 | ±41 |
| | o Emission to air from end-use | 13,200 | ±41 |
| | o Quantity landfilled | 1,400 | ±99 |
| Adhesives | Total solvent used in adhesives | 19,800 | ±20 |
| | Methyl chloroform used to clean vessels from solvent based adhesives | 1,430 | +30/-50 |
| | o Solvent to air from vessel cleaning | 210 | +39/-56 |
| | o Solvent reclaimed by outside services | 735 | +40/-64 |
| | o Still bottom incinerated | 45.5 | +40/-64 |
| | o Incinerator air emissions | 2.28 | +89/-100 |
| | o Methyl chloroform destroyed | 43.2 | +40/-64 |

| Process/Operation | Waste | Quantity (kkg) | Uncertainty (%) |
|---|---|---|---|
| Adhesives (cont.) | | | |
| | o Solvent reclaimed in-house | 161 | +46/-61 |
| | o Still bottoms landfilled | 17.9 | +46/-61 |
| | o Solvent discharged | 238 | +49/-57 |
| | Methyl chloroform in solvent-based adhesive products | 15,400 | ±15 |
| | o Releases to air from production | 77.0 | +52/-25 |
| | o Releases to air from end-use | 14,600 | ±16 |
| | o Releases to land | 766 | ±76 |
| | Methyl chloroform used to clean vessels from water-based adhesives | 537 | +30/-50 |
| | o Quantity emitted to air | 80.6 | +39/-56 |
| | o Quantity reclaimed by outside contractor | 282 | +40/-64 |
| | o Quantity of still bottoms incinerated | 14.8 | +40/-64 |
| | o Incinerator air emissions | 0.740 | +89/-100 |
| | o Methyl chloroform destroyed | 14.1 | +40/-64 |
| | o Quantity reclaimed in-house | 61.6 | +46/-61 |
| | o Quantity of still bottoms landfilled | 6.85 | +46/-61 |
| | o Quantity discharged | 91.3 | +49/-57 |
| | Methyl chloroform in water-based adhesive products | 2,560 | ±75 |
| | o Emissions to air from production | 13 | +90/-78 |

| Process/Operation | Waste | Quantity (kkg) | Uncertainty (%) |
|---|---|---|---|
| Adhesives (cont.) | | | |
| | o Emissions to air from end-use | 2,440 | ±76 |
| | o Emissions to land | 129 | +106/-99 |
| Textiles | Average use of methyl chlorofirm for scouring per plant | 3.06 | +58/-42 |
| | Total methyl chloroform used for scouring | 1,940 | +59/-43 |
| | o Quantity evaporated to air | 1,920 | +59/-43 |
| | o Quantity remaining in water | 1.94 | +62/-47 |
| | o Quantity absorbed in sludge | 17.5 | +62/-47 |
| | Total methyl chloroform used for cleaning | 987 | ±96 |
| | o Quantity evaporated to air | 987 | ±96 |
| | Methyl chloroform volatilized during dyeing operations | 10 | ±56 |
| Drain Cleaners/ Septic Tank Cleaners | Methyl chloroform used in drain and septic tank cleaners | 1,500 | +75/-50 |
| | Total methyl chloroform in septic tank cleaners | 1,200 | +75/-50 |
| | o Releases to air from evaporation | 60 | +90/-71 |
| | o Quantity retained in sludge | 285 | +92/-100 |

| Process/Operation | Waste | Quantity (kkg) | Uncertainty (%) |
|---|---|---|---|
| Septic Tank Cleaners (cont.) | o Quantity released to groundwater | 855 | +78/-64 |
| | Total methyl chloroform in drain cleaners | 300 | +75/-50 |
| | o Quantity evaporated/ sewered homes | 11.3 | +110/-94 |
| | o Quantity discharged/ sewered homes | 214 | +75/-50 |
| | o Quantity evaporated/ homes with septic tanks | 3.75 | +90/-71 |
| | o Quantity retained in sludge/homes with septic tanks | 18 | +96/-10 |
| | o Quantity released to groundwater | 53 | +78/-64 |
| Paints | Methyl chloroform used in paint industry | 5,000 | +106/-99 |
| | o Quantity emitted to air | 4,950 | +106/-99 |
| | o Quantity emitted to wastewater | $1.08 \times 10^{-4}$ | ±57 |
| | o Quantity emitted to land | 100 | +106/-99 |
| Inks | Methyl chloroform used in inks | 2,840 | ±75 |
| | o Quantity emitted to air | 2,780 | ±75 |
| | o Quantity emitted to land | 56.8 | +124/-99 |

| Process/Operation | Waste | Quantity (kkg) | Uncertainty (%) |
|---|---|---|---|
| Film Cleaning | Total methyl chloroform used in film cleaning | 220 | ±58 |
| | o Quantity emitted to air | 218 | ±58 |
| | o Quantity emitted to land | 2.2 | +114/-99 |
| Pharmaceuticals | Methyl chloroform emitted to air from extractions | 124 | +98/-100 |
| | o Quantity landfilled | 20.7 | +98/-100 |
| | o Quantity incinerated/ destroyed | 177 | +84/-100 |
| | o Incinerator air emissions | 9.32 | +116/-100 |
| Leather Tanning | Methyl chlorofrom volatilized from finishing process | 104 | ±99 |
| | o Quantity discharged to wastewater | 1.88 | ±42 |

## 7.0 DATA GAPS AND RECOMMENDATIONS

This section presents a brief description of the types of data needed to "fine tune" the materials balance for methyl chloroform. Further data acquisition should emphasize the major uses of methyl chloroform. Because methyl chloroform used in cleaning, adhesives and aerosols accounts for over 80 percent of the total U. S. production, and 86 percent of the total actually used in the United States in 1978 (6 percent was stockpiled and 6 percent was exported), accurate data on these end uses is important.

For minor end uses such as the leather tanning industry, the pharmaceutical industry, film cleaning and catalyst preparation, where cumulatively less than one percent of the methyl chloroform is used, the overall materials balance would not be significantly improved by obtaining additional information on these end uses.

In the discussion which follows, major data gaps and uncertainties are discussed for each end use and recommendations are made as to how this data could be be obtained.

### 7.1 Methyl Chloroform Production With the Vinylidene Chloride Method

There are few data gaps in the production process of methyl chloroform from vinylidene chloride.

The actual flow diagram of the vinylidene chloride-based production process was not obtained and thus an accurate evaluation potential emission source was not possible. This information can be obtained if the producer is willing to provide a simplified flow diagram of the process.

Emissions of methyl chloroform from this process were estimated based on a derived flow diagram of the process. If a simplified flow diagram of the actual process and emission factors from appropriate sources were provided, these revised estimates could be evaluated and the materials balance corrected as necessary.

For future considerations, the vinylidene chloride method does not warrant more in-depth studies since Pittsburgh Plate Glass (PPG) placed this process on standby in late 1978. The newly developed production process for methyl chloroform in 1979 (see Section 2.4) probably uses vinyl chloride as the raw material. Thus, it will be worthwhile to study this new production process in future tasks. Information confirming the production process and estimating emission quantities from this new process should be gathered for further studies. If the new process is vinyl chloride-based, emissions factors from the Dow facilities (Section 2.2) could be used as an interim method for a 1979 materials balance.

The quantity of methyl chloroform produced in 1978 via this process was not known, and was estimated using the percentage obtained for 1976. This presents an uncertainty which could affect the entire materials balance of methyl chloroform produced by the vinylidene chloride method.

Since relatively small quantities of methyl chloroform are released by this process (<.02 percent of total production), the importance of monitoring plant releases is minimal. For example, previous monitoring efforts have shown water emissions to be in ppb.

## 7.2 Vinyl Chloride Process

The vinyl chloride process has been described by both Dow Chemical Company and Hydroscience, Inc. (Dow, 1979, Hydroscience, 1979). Since the process is known and emission factors have been provided in the literature, there are no data gaps.

To improve the uncertainty of the emission values, proprietary data must be obtained and air and solid waste monitoring must be performed. Production data is reported to the Department of Commerce annually. This information should be obtained from Dow or the Department of Commerce to provide a better estimate of the total methyl chloroform production and, subsequently, better emission estimates.

Emissions to the environment were calculated using emission factors provided by Hydroscience, Inc. and through various other indirect methods. Except for emissions from product storage and handling, the request for information from Dow's proprietary records or the monitoring of their facility would have relatively little value. The emissions from these sources within the Dow plant are insignificant (0.01%) when compared to other emission sources. For example, previous water effluent monitoring has resulted in quantities measuring in the ppb.

Emission factors from product storage and handling should be verified. Either information from Dow's monitoring records or EPA monitoring would be necessary to improve the accuracy of these values. An alternative method would be to review the filling and emptying processes and the quantities transferred for both storage and handling of methyl chloroform. Also, the quantities stored and the length of time in storage, would permit the calculation of more accurate emission factors (see Appendix F).

### 7.3 Ethane Process

Ethane process has been described by Hydroscience, Inc. (Hydroscience, 1979). Since the process for a model plant is known and emission factors have been provided in the literature, there are no data gaps.

To improve the uncertainty of the emission values, proprietary data must be obtained and monitoring must be performed. Production data is reported to the Department of Commerce annually. This information should be obtained from Vulcan or the Department of Commerce to provide a better estimate of the total methyl chloroform production and, subsequently, better emissions estimates.

Emissions to the environment were calculated using emission factors provided by Hydroscience, Inc. and through various indirect methods. Except for emissions from product storage and handling, the request for information from Vulcan's proprietary records or the monitoring of their facility would have relatively little value. The emissions from these sources within the Vulcan plant are insignificant (<0.001%) when compared to other emission sources.

Emission factors from product storage and handling should be verified. Either information from Vulcan's monitoring records or EPA monitoring would be necessary to improve the accuracy of these values. An alternative method would be to review the filling and emptying processes and the quantities transferred for both storage and handling of methyl chloroform. Also, the quantities stored and the length of time in storage, would permit the calculation of more accurate emission factors (see Appendix F).

## 7.4 Metal Cleaning

Our estimate for the total methyl chloroform losses from the metal cleaning industry, are probably as accurate as one could hope to obtain; this estimate was based on survey results and industrial contacts, and has accounted for solvent substitution for trichloroethylene.

We are somewhat less confident, however, of our estimates for the various methods of environmental release. Our highest degree of uncertainty is for the estimates made for total waste solvent, especially from cold cleaning, and for the ultimate disposal of waste solvent (whether landfilled or discharged). Because air emissions were calculated by subtracting the difference between total emissions and waste solvent, this uncertainty is transferred to our estimates for air emissions, as well. These uncertainties are due to varying data on the extent to which solvent recovery is practiced, the extent to which good housekeeping practices are enforced(i.e., use of covers) and the variable nature of solvent degreasing operations. Similar uncertainties were also expressed by

OAQPS (1977) which had several support studies available to them, including the Dow survey results. This suggests that these uncertainties probably cannot be resolved. A higher degree of confidence in our estimates, could be obtained, however, if manufacturers of solvent degreasers could review the estimates and assumptions used in calculating environment losses.

Small operations are the biggest problem in assessing emissions from the metal cleaning industry. There are thousands of small metal cleaners throughout the United States. These operations may account for as much as 50 percent of the total methyl chloroform used in metal cleaning. Without a detailed survey of all operations, the emission estimates presented in this report can only be considered as accurate as the large uncertainties placed upon them.

## 7.5 Aerosols

The quantity of methyl chloroform consumed in the production of aerosol products is estimated by many information sources; such as SRI and Chemical Marketing Reports. Thus, the uncertainty assigned to this figure is very small.

The estimated emissions of methyl chloroform from the consumption of aerosol products was less certain since it depends greatly on the general usage and habits of consumers. Emissions from the production phase were estimated based on the information obtained from experts in the aerosol production field. Therefore, the uncertainty of this figure is correspondingly small.

We are confident that emissions estimates of methyl chloroform from the production and consumption of aerosol products are accurate to within the given uncertainties. These estimates assume the consumption of methyl chloroform in aerosol products does not deviate from that reported herein.

A study should be undertaken to identify the average quantity of aerosol products remaining in a can which has been disposed. The percentage of methyl chloroform remaining in landfilled containers could be more accurately defined.

## 7.6 Adhesives

There are few data gaps on the use of methyl chloroform in the adhesives industry, but there are several areas where the uncertainty of our estimate is significant. The estimate of total methyl chloroform used by the adhesives industry is considered to be reasonably accurate, since this was verified by industry. Percentage distribution of methyl chloroform losses betewen solvent based and water based adhesives is also considered accurate. However, a more accurate estimate of the amount of solvent used in cleaning vessels is considered important. Although the amount of solvent used for this purpose is less than 5 percent, these losses can be easily controlled with solvent recovery practices. Furthermore, in geographic areas where adhesive industries are highly concentrated (the Northeast, Texas, and the Great Lakes area) good housekeeping practices would eliminate these areas as possible "Hot Spots". Although we have assumed that solvent recovery is widely practiced, quantitative information is needed.

Since more than 95 percent of all solvent losses are from product use, we need to specify the quantities of methyl chloroform used in various types of adhesives and their specific end uses. In certain end uses, such as the manufacture of pressure sensitive tapes, solvent recovery is practiced. Conversely, solvent losses from household use of solvent based adhesives are uncontrolled. These end use emissions may vary widely.

Ideally, an industry-wide survey could be made to determine solvent cleaning practices and to quantify the methyl chloroform used in solvent based adhesives. An industry review of the assumptions used in arriving at the estimates included herein might be adequate to "fine tune" the materials balance.

## 7.7 Textiles

Emission and consumption quantities of methyl chloroform used for textile were not obtained during the preparation of this report. The quantities presented in this report were all estimated based on very scattered data provided by textile trade associations.

The following recommendations are suggested in order to gather more information on this category: a) a survey should be done on the amount of methyl chloroform used by many major textile plants and/or the quantity of methyl chloroform sold to all the textile establishments in the United States; the latter can be obtained if the major producers are willing to provide the information; b) the information on the process in which the chemical is used and the waste treatment facilities of representative textile establishments should be made available.

## 7.8 Paints

Methyl chloroform use in the paint industry is limited to traffic paints (verified by references and verbal communication with major paint manufacturers). The total quantity used is known to be extremely small. Exact quantification might be obtained by contacting or surveying a representative sample from among the 1,500 paint manufacturers, but this effort does not seem justified for such a small use.

The assumption that 98 percent of the methyl chloroform used in paints is emitted directly to the atmosphere is considered reliable due to the method of application of traffic paints.

## 7.9 Inks

Although industrial contacts were made to identify the amount of methyl chloroform used in inks and ink cleaning products, JRB was not able to obtain quantitative data. Written requests for quantitative information should be made to manufacturers of those products (see Appendix D). Also, efforts should be made to quantify the amount used in this industry as a grease cutter. Considering the small quantity of methyl chloroform estimated to be used in inks and related products, a study to quantify methyl chloroform used in presently unidentified products would not contribute significantly to the overall methyl chloroform materials balance.

## 7.10 Septic Tank Cleaners and Drain Cleaners

There is a total lack of quantitative data on the use of septic tank cleaners and drain cleaners containing methyl chloroform. Estimates made for this material balance were determined by assuming a "reasonable use" of these products among home owners. Quantitative information on the use of these products is important because once methyl chloroform is discharged into the groundwater, there is no opportunity for it to degrade. The information needed to quantify methyl chloroform used in these products in 1978 could be obtained by doing a nationwide consumer product survey. Also, since some of these products have been taken off the market in recent years, an estimate of the methyl chloroform which has accumulated in groundwater would require all previous sales figures.

## 7.11 Methyl Chloroform Used in the Preparation of Catalysts

The information on the quantity of methyl chloroform used in this category does not exist anywhere in the literature. We expect that the quantity of methyl chloroform used for the preparation of catalysts does not contribute significantly to the total consumption of this chemical, thus any further investigations on this subject are not worthwhile.

## 7.12 Film Cleaning

The major users of methyl chloroform as a film cleaner have been identified. Although an estimate was required to account for minor users, JRB is confident that the total use of methyl chloroform in this application is very small and that the estimate made is reasonably accurate. The information that would be gained by tracking down all other users would not be worth the time invested since only about 0.1 percent of all methyl chloroform produced is used in film cleaning. Because of the small amount of methyl chloroform used and the method of application, the assumption that 99 percent of the solvent is lost to the air is considered accurate.

## 7.13 Leather Tanning

Although no quantitative data was available on the amount of methyl chloroform used in leather tanning, use in this industry is known to be very small. The estimate made for this materials balance was based on information from contacts and our knowledge of the use of solvent in this industry. Although these estimates are not expected to be more accurate than ±50 percent, an industry survey would be required to quantify end uses more accurately. The information that would be obtained by such a survey would not contribute significantly to the overall materials balance since the quantity of methyl chloroform used by this industry is so small.

## 8.0 DISCUSSION OF NATIONAL ACADEMY OF SCIENCE STUDY OF OZONE DEPLETION BY HALOCARBONS

The objective of this chapter is to discuss the results of the recently published National Academy of Science study on Stratospheric Ozone Depletion by Halocarbons, as it relates to methyl chloroform (NAS, 1979). The impact of methyl chloroform on ozone depletion was not the major emphasis in the NAS study and consequently methyl chloroform is only discussed generally.

### 8.1 Comparison of Production Estimates

Global production estimates for 1977-1982 were derived from 1976 data obtained by Detrex Corporation, a major manufacturer of metal cleaning equipment. At that time, it was projected that 1977 production would approximate 587,000 kkg and that growth would average 10 percent from 1977 to 1979 and 5 percent from 1979 to 1982. At this rate, 1982 production would approximate 853,000 kkg (McConnell and Schiff, 1978). Detrex was contacted to determine how these estimates were made. Dr. McCracken of Detrex indicated that this estimate was made in 1976 and was based on global production capacity and on projections for a "booming" market for methyl chloroform in the coatings industry (McCracken, 1979). Dr. Harold Schiff, Chairman of the NAS committee on Impacts of Stratospheric Change also indicated that the estimates used in the NAS study were based on capacity and not on actual production (Schiff, 1978).

In 1976, it was anticipated that methyl chloroform would capture the United States market loss by trichloroethylene and perchloroethylene as a result of Los Angeles' Rule 66 and similar regulations enacted in other states concerning photochemical oxidation. However, both Dr. McCracken (McCracken, 1979) and a recently published article in Chemical and Engineering News indicated that the market has not "taken off" as was expected. However, NIOSH regulations and potential regulations under Section III of the Clean Air Act Amendments have encouraged industries to phase out use of methyl chloroform. Several industrial contacts which were made during the Level II materials balance for methyl chloroform, supported the contention that the market has not grown as expected. Hercules, which sells resins to adhesive manufacturers indicated that their clients are phasing out solvents-based adhesives and substituting with "hot-melts" and water based adhesives (Hercules, 1979). Contacts with UPACO and Mobay Chemicals, which formulate adhesives indicated that they are anticipating regulations on all chlorinated solvents (UPACO, 1979; Mobay, 1979). They are not interested in substituting methyl chloroform for trichloroethylene because they feel that it will eventually be regulated as well. NIOSH regulations an data on the carcinogenicity of methyl chloroform have also been influential in encouraging the adhesives industry to phase out the use of methyl chloroform. Similar sentiment was expressed by contacts in the textile industry. Contacts of the Wool Bureau and the Institute of Textile Technology indicated that they are also phasing out chlorinated solvents in anticipation that they will be regulated.

In this materials balance study, JRB had used a 1977 global production estimate of 427,000 kkg or 73 percent of the NAS estimate. This figure was approximated by the Dow Corporate Product Development (Neely and Agin, 1978). Dr. McCracken indicated the the 1976 projections made by Detrex have not been realized and that the production estimates made by the DOW Corporated Product Department are probably correct (McCracken, 1979). In a recently held conference on methyl chloroform (EPA, 1979d), DOW speculated an average annual increase in methyl chloroform production of 6 percent (Farber, 1979c). DOW indicated that they expect peaks and valleys in production and the uncertainty of their 6 percent estimate is ± 100 percent. It does not seem likely that the growth rate would exceed DOW's estimates for the following reason. In 1978, the United States produced nearly 60 percent of the methyl chloroform produced globally. Between 1976 and 1977, U. S. production increased by only 1 percent. Between 1978 and 1979, the growth rate declined by 2 percent. To attain a growth rate of 6 percent annually, production outside the United States would need to increase at about 15 percent/year. Therefore, this growth rate is consistent with the growth rate projected in the NAS study (NAS, 1979).

If the 1977 global production estimate of 427, 000 kkg was more accurate than the NAS estimate of 587,000 kkg then production in 1982 may be substantially lower than NAS predicted. Assuming two unique scenarios, where average production increases by 6 percent and 10 percent respectively, Table 8.8-1 shows that 1982 production would be in the range of 572 - 689 x $10^3$ kkg or 67 - 81 percent of the NAS estimate.

Table 8.1-1 Estimated Global Production of Methyl Chloroform From 1977-1982 Using Three Possible Scenarios (kkg x $10^3$)

| Year | JRB Estimate 6% Growth | JRB Estimate 10% Growth | NAS Estimate |
|---|---|---|---|
| 1977 | 427 | 427 | 587 |
| 1978 | 453 | 470 | - |
| 1979 | 480 | 517 | 707 |
| 1980 | 509 | 569 | - |
| 1981 | 540 | 626 | - |
| 1982 | 572 | 689 | 853 |

SOURCE: NAS, 1979 (Taken from McConnell and Schiff).
JRB, based on estimate from Dow Corp. Product Dept. and Dow estimate for growth.

## 8.2 Discussion of Estimates for Ozone Depletion

The NAS study also compared the impact of methyl chloroform on stratospheric ozone depletion to that of F-11 and F-12. The study predicted that, based on 1976 production figures, methyl chloroform destroys 8 to 15 percent of the ozone destroyed by F-11 and F-12. Using the half-lifes of of these halocarbon estimated in the study and 1976 production data, this estimate is accurate.

NAS also predicted that in 1982, destruction of ozone by methyl chloroform will be 20 percent greater than the amount destroyed by F-11 and F-12. This estimate is unreasonably high and there is some question about the accuracy and clarity of this statement. We have clarified this error with NAS Chairman, Dr. Harold Schiff. It seems that an incorrect estimate of 1982 production was used for this calculation. It was assumed that 1982 production was 16 x $10^5$ kkg, nearly twice the production estimated earlier in the document (853 x $10^3$ kkg).

JRB has made an independent estimate of the percentage of ozone destroyed by methyl chloroform in comparison to F-11 and F-12, 1982. Global production estimates for methyl chloroform of 852 x $10^3$ kkg and 572 x $10^3$ kkg were considered.

A half-life of 8-12 years, 70 years, and 110 years was used for methyl chloroform, F-11 and F-12, respectively (NAS, 1979). Based on these half-lives, it was estimated that between 10 and 20 percent of the methyl chloroform molecules reach the stratosphere, and 80 percent of the F-11 molecules and 90 to 100 percent of the F-12 molecules reach the stratosphere. It was also assumed that production of F-11 and F-12 would remain constant until 1982, at 331 kkg and 424 kkg, respectively. Then the ratio of ozone destroyed by F-11 and F-12 as compared to methyl chloroform is calculated by multiplying the ratio of half-lives times the ratio of production estimates times the ratio of chlorine atoms.

Assuming 852 x $10^3$ kkg is an accurate estimate of 1982 global production

For F-11

0.8/0.15 x 331 x $10^3$ kkg/852 x $10^3$ kkg x 3 Cl/3 Cl = 2.1:1

For F-12

1.0/0.15 x 424 x $10^3$ kkg/852 x $10^3$ kkg x 2 Cl/3 Cl = 2.2:1

TOTAL 4.3:1

The estimated percentage of ozone destroyed by methyl chloroform as compared to F-11 plus F-12 is 23 percent, if 1982 methyl chloroform production approximates 852 x $10^3$ kkg.

Assuming 527 x $10^3$ kkg is more representative of 1982 production figures, then:

For F-11

0.8/0.15 x 331 x $10^3$ kkg/527 x $10^3$ kkg x 3 Cl/3 Cl = 3.3:1

For F-12

1.0/0.15 x 424 x $10^3$ kkg/527 x $10^3$ kkg x 2 Cl/3 Cl = 3.6:1

TOTAL 6.9:1

Then, assuming 1982 global production of 527 x $10^3$ kkg, methyl chloroform would destroy about 14 percent as much ozone as F-11 and F-12.

Based on JRB's calculations, ozone depletion by methyl chloroform in 1982 will be 14-23 percent of that destroyed by F-11 and F-12.

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# APPENDIX A

## PROCESS DESCRIPTIONS

(Sources: Hydroscience, 1979 and EPA 1979a)

### A.1 Introduction

The processes for producing methyl chloroform from vinyl chloride, from ethane and from vinylidene chloride are described.

In 1978, most of the methyl chloroform produced domestically is made by the vinyl chloride process, with lesser amounts made by the vinylidene chloride and ethane processes. Vinyl chloride, which is produced from ethylene dichloride, is first hydrochlorinated with hydrogen chloride to 1,1-dichloroethane, which is then thermally chlorinated to produce methyl chloroform. The yields from vinyl chloride are over 95%.

With ethane and chlorine as raw materials, methyl chloroform is produced by the noncatalytic chlorination of ethane. Ethyl chloride, vinyl chloride, vinylidene chloride, and 1,1-dichloethane are also produced, with the relative quantities of the various product fractions being somewhat dependent on operating conditions. When methyl chloroform is the only desired product, vinyl chloride and vinylidene chloride are hydrochlorinated to 1,1-dichloroethane and methyl chloroform respectively, and ethyl chloride and 1,1-dichloroethane are recycled to the chlorination step.

Methyl chloroform is produced directly from vinylide chloride by hydrochlorination and distillation. Yields from vinylidene chloride are approximately 98%.

## A.2 Vinyl Chloride Process

Starting with vinyl chloride the following reactions are required to produce methyl chloroform: the hydrochlorination of vinyl chloride to 1,1-dichloroethane and the chlorination of 1,1-dichloroethane to methyl chloroform. The hydrochlorination of vinyl chloride to 1,1-dichloroethane takes place according to the following reaction:

$$\underset{\text{(vinyl chloride)}}{CH_2{=}CHCl} \quad + \quad \underset{\text{(hydrogen chloride)}}{HCl} \xrightarrow{FeCl_3} \underset{\text{(1,1-dichloroethane)}}{CH_3{-}CHCl_2}$$

The chlorination of 1,1-dichloroethane to methyl chloroform takes place according to the following reaction:

$$\underset{\text{(1,1-dichloroethane)}}{CH_3{-}CHCl_2} \quad + \quad \underset{\text{(chlorine)}}{Cl_2} \longrightarrow \underset{\text{(methyl chloroform)}}{CH_3{-}CCl_3} \quad + \quad \underset{\text{(hydrogen chloride)}}{HCl}$$

Figure A-1 represents a flow diagram for a process in which methyl chloroform is produced from vinyl chloride. Vinyl chloride (stream 1) from storage, hydrogen chloride (stream 2), and the recycled overhead stream (7) from the light-ends column are fed to the hydrochlorination reactor. The reaction is exothermic and takes place at 35 to 40°C in the presence of a catalytic amount of ferric chloride.

Ammonia (stream 4) is added to the reactor effluent (stream 3), forming a solid complex with the residual hydrogen chloride and the ferric chloride catalyst. The complex is removed by the spent catalyst filter as a semisolid waste stream (source G). The filtered hydrocarbon stream (stream 5) passes to the heavy-ends column, where high-boiling chlorinated organics (tars) are removed as a waste stream (source H) from the bottom.

The overhead (stream 6) passes to the light-ends column, where a separation is made between 1,1-dichloroethane and the lighter components,

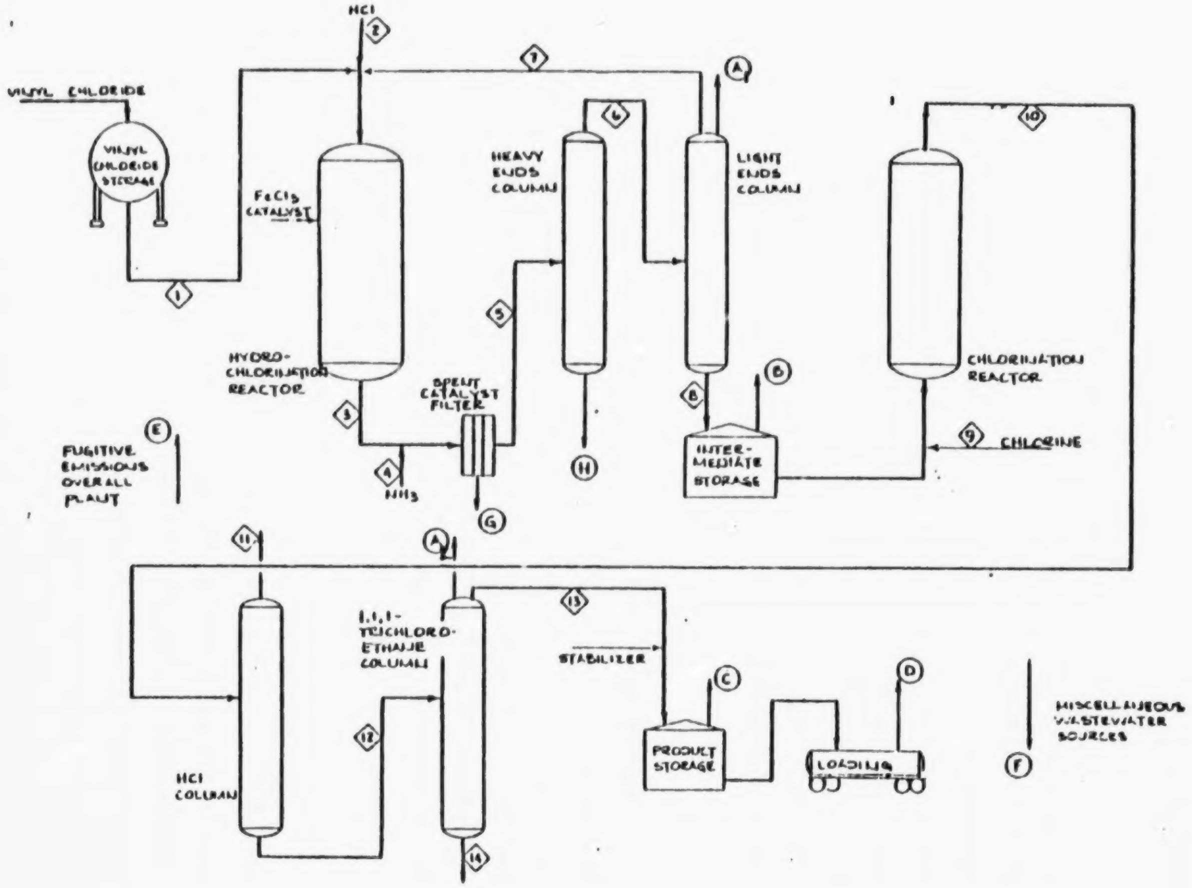

VINYL CHLORIDE
VINYL CHLORIDE STORAGE
1
HCl
2
7
A
FeCl3 CATALYST
HYDRO-CHLORINATION REACTOR
3
4
NH3
SPENT CATALYST FILTER
G
5
HEAVY ENDS COLUMN
H
6
LIGHT ENDS COLUMN
8
B
INTER-MEDIATE STORAGE
10
CHLORINATION REACTOR
9
CHLORINE
FUGITIVE EMISSIONS OVERALL PLANT
E
11
A
HCl COLUMN
12
1,1,1-TRICHLORO-ETHANE COLUMN
13
14
STABILIZER
PRODUCT STORAGE
C
LOADING
D
MISCELLANEOUS WASTEWATER SOURCES
F

Fig. A-1. Flow Diagram for Methyl Chloroform from Vinyl Chloride primarily unreacted vinyl chloride. The overhead stream (7) is recycled to the hydrochlorination reactor. The 1,1-dichloroethane product is removed as the bottom stream (8) and transferred to intermediate storage.

1,1-Dichloroethane from intermediate storage and chlorine (stream 9) are combined and fed to the chlorination reactor, where the 1,1-dichloroethane is converted to methyl chloroform. The reaction is exothermic and noncatalytic, occurring at a temperature of about $400^{\circ}$ C. The reactor effluent (stream 10) passes to the hydrogen chloride column, where the hydrogen chloride formed in the reaction and some low-boiling organic compounds are removed overhead (stream 11). This stream may be used to supply the hydrogen chloride requirements of other chlorinated organic processes directly (e.g., the ethylene dichloride process) or it may be purified to remove the contained organics before it is used.

The bottom stream (12) from the hydrogen chloride column passes to the methyl chloroform column. The purified product is removed overhead (stream 13) and, after the addition of a stabilizer, is transferred to storage. The bottom stream (14) from the methyl chloroform column, composed primarily of 1,1,2-trichloroethane, is transferred as feed to other chlorinated organic processes (e.g., perchloroethylene-trichloroethylene).

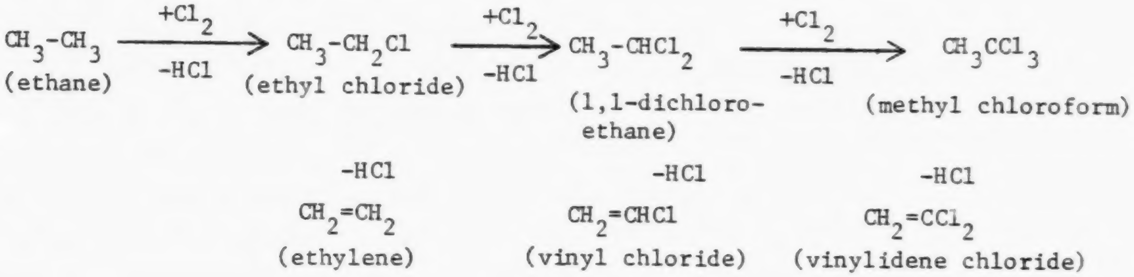
The distillation column vents (A), which release primarily noncondensable gases, are sources of process emissions. Storage emissions (vents B and C) include emissions from intermediate storage of 1,1-dichloroethane and from methyl chloroform product storage. Handling emissions (source D) result from the loading of methyl chloroform into tank trucks or tank cars for shipment.

Fugitive emissions (E) occur when leaks develop in valves or compressor seals. When process pressures are higher than the cooling-water pressure, VOC can leak into the cooling water and escape as a fugitive emission from the cooling towers.

Secondary emissions can occur when wastewater from miscellaneous process sources (source F) is sent to a wastewater treatment system and the contained VOC are desorbed. Other sources of secondary emissions are from the disposal of catalyst residue (source G) in landfill and from the combustion of organic wastes (source H). (Secondary emissions occur when VOC are emitted with the combustion flue gas.)

## A.3 Ethane Process

When chlorine is reacted with ethane, the main sequence of reactions occurring can be summarized as follows:



$$\begin{array}{ccccccc} CH_3\text{-}CH_3 & \xrightarrow[-HCl]{+Cl_2} & CH_3\text{-}CH_2Cl & \xrightarrow[-HCl]{+Cl_2} & CH_3\text{-}CHCl_2 & \xrightarrow[-HCl]{+Cl_2} & CH_3CCl_3 \\ \text{(ethane)} & & \text{(ethyl chloride)} & & \text{(1,1-dichloro-ethane)} & & \text{(methyl chloroform)} \\ & & -HCl & & -HCl & & -HCl \\ & & CH_2{=}CH_2 & & CH_2{=}CHCl & & CH_2{=}CCl_2 \\ & & \text{(ethylene)} & & \text{(vinyl chloride)} & & \text{(vinylidene chloride)} \end{array}$$

Minor quantities of 1,2-dichloroethane and 1,1,2-trichloroethane are also produced. The product mix attained can be varied somewhat through changes in operating conditions. When methyl chloroform is the only desired product, the ethyl chloride and 1,1-dichloroethane produced are recycled to the chlorination reactor, and the vinyl chloride and vinylidene chloride are catalytically hydrochlorinated to 1,1-dichloroethane and methyl chloroform respectively, as represented by the following reactions:

$$\mathrm{CH_2{=}CHCl} + \mathrm{HCl} \xrightarrow{\mathrm{FeCl_3}} \mathrm{CH_3{-}CHCl_2}$$

(vinyl chloride) (1,1-dichloroethane)

$$\mathrm{CH_2{-}CCl_2} + \mathrm{HCl} \xrightarrow{\mathrm{FeCl_3}} \mathrm{CH_3{-}CCl_3}$$

(vinylidene chloride) (methyl chloroform)

Figure A-2 represents a flow diagram for an ethane chlorination process. For startup, ethane is circulated through the chlorination reactor and through a fuel-fired furnace (not shown) to bring the reactor temperature to about 350° C before normal feed flows are established. Chlorine (stream 1) and ethane (stream 2) supplied by pipeline are then fed to the reactor. The approximate chlorination reaction conditions are a temperature of 400° C and a pressure of 600 kPa. The reactor is operated adiabatically with a residence time of about 15 sec. A catalyst is not required for the chlorination reaction. When recycle flows are established, the 1,1-dichloroethane and ethyl chloride formed in the process (12 and 19) are also introduced as chlorination reactor feed.

The exit stream (3) from the reactor contains ethane, ethylene, vinyl chloride, ethyl chloride, vinylidene chloride, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,2-trichloroethane, methyl chloroform, a small amount of other chlorinated hydrocarbons, and hydrogen chloride.

The reactor effluent gas (stream 3) enters the quench column, where it is cooled and a residue stream consisting primarily of tetrachloroethane and hexachloroethane is removed (source H).

The overhead stream (4) from the quench column enters the hydrogen chloride column for separation of ethane, ethylene, and hydrogen chloride from the chlorinated hydrocarbons. A part of the hydrogen chloride column overhead stream (5) supplies the hydrogen chloride requirements

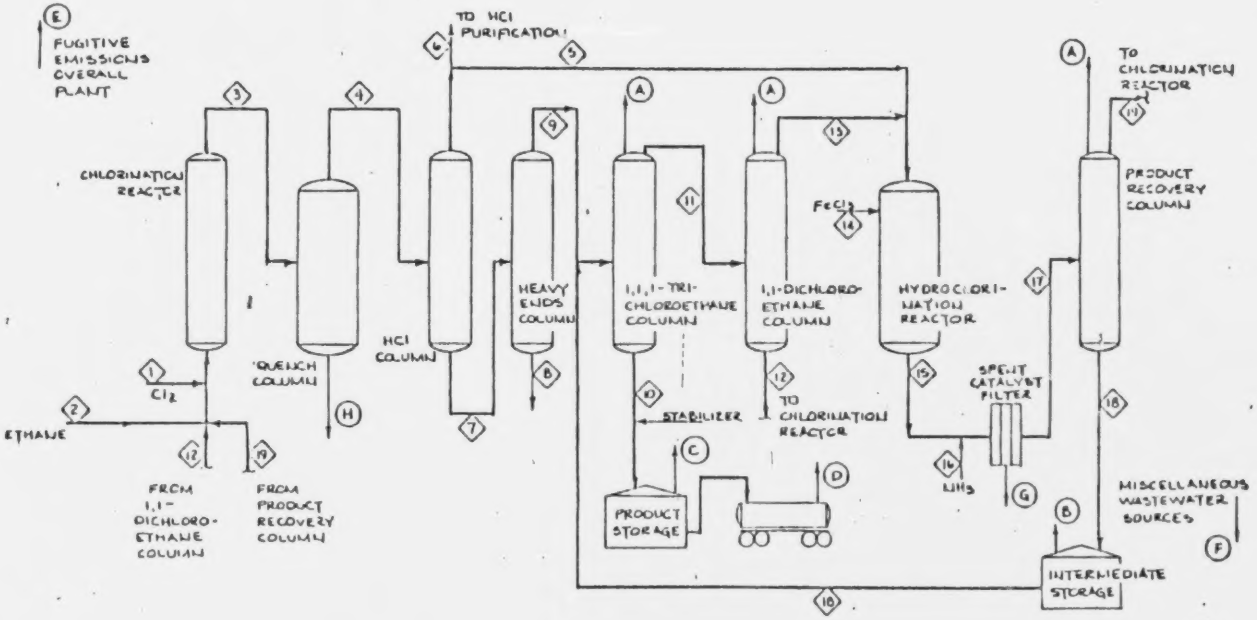

E
FUGITIVE EMISSIONS OVERALL PLANT
CHLORINATION REACTOR
1
$Cl_2$
2
ETHANE
12
FROM 1,1-DICHLORO-ETHANE COLUMN
19
FROM PRODUCT RECOVERY COLUMN
3
QUENCH COLUMN
H
4
HCl COLUMN
6
TO HCl PURIFICATION
5
7
HEAVY ENDS COLUMN
8
9
A
1,1,1-TRI-CHLOROETHANE COLUMN
10
STABILIZER
C
PRODUCT STORAGE
D
11
A
1,1-DICHLORO-ETHANE COLUMN
12
TO CHLORINATION REACTOR
13
$FeCl_3$
14
HYDROCLORI-NATION REACTOR
15
16
$NH_3$
SPENT CATALYST FILTER
G
17
A
TO CHLORINATION REACTOR
19
PRODUCT RECOVERY COLUMN
18
B
INTERMEDIATE STORAGE
18
MISCELLANEOUS WASTEWATER SOURCES
F

Figure A-2. Flow Diagram for Methyl Chloroform from Ethane of the hydrochlorination reactor. The excess hydrogen chloride and the contained ethane and ethylene (stream 6) pass to a hydrogen chloride purification step (not shown), eventually providing hydrogen chloride for other processes.

The hydrogen chloride-free chlorinated hydrocarbons (stream 7) from the hydrogen chloride column pass to the heavy-ends column, where the higher boiling components (primarily 1,2-dichloroethane and 1,1,2-trichloroethane) are removed as a bottoms stream (8) and are transferred as feed to other chlorinated hydrocarbon processes (e.g., perchloroethylene). The overhead stream (9), composed primarily of methyl chloroform vinyl chloride, vinylidene chloride, ethyl chloride, and 1,1-dichloroethane, is combined with the bottoms stream (18) from the product recovery column and fed to the methyl chloroform column. Refined methyl chloroform is transferred to product storage.

The overhead stream (11) from the methyl chloroform column is fed to the 1,1-dichloroethane column, where 1,1-dichloroethane is separated as the bottoms stream (12) and is recycled as feed to the chlorination reactor. The overhead stream (13), composed of vinyl chloride, vinylidene chloride, and ethyl chloride, is fed to the hydrochlorination reactor, where vinyl chloride is converted to 1,1-dichloroethane and vinylidene chloride is converted to methyl chloroform. Hydrogen chloride requirements are supplied by a part of the hydrogen chloride column overhead stream (stream 5). Hydrochlorination reactor conditions include a temperature of $65^{\circ}$ C, a pressure 450 kPa, and a catalytic amount of ferric chloride (stream 14).

Ammonia (stream 16) is added to the reactor effluent stream (stream 15) and reacts with the residual hydrogen chloride and ferric chloride to form a solid ammonium chloride—ferric chloride—ammonia complex. The solid complex is removed by the spent catalyst filter as a semisolid waste stream (source G). The filtered hydrocarbon stream (17) passes to the product recovery column, where a rough separation of methyl chloroform from the 1,1-dichloroethane—ethyl chloride fraction is made. The bottoms fraction (stream 18), composed primarily of methyl chloroform, is recycled to the methyl chloroform column. The overhead stream (19), consisting primarily of ethyl chloride and 1,1-dichloroethane, is recycled to the chlorination reactor.

The distillation column vents (A), which release primarily noncondensable gases, are the only significant source of process emissions. Storage emission sources (vents B and C) include intermediate storage and product storage. Handling emissions (vent D) result from the loading of methyl chloroform into tank cars and tank trucks.

Fugitive emissions (E) occur when leaks develop in valves or in pump seals. When process pressures are higher than the cooling-water pressure, VOC can leak into the cooling water and escape as a fugitive emission from the cooling towers.

Secondary emissions can occur when wastewater from miscellaneous process sources (source F) is sent to a wastewater treatment system and the contained VOC are desorbed. Other sources of secondary emissions are from the disposal of catalyst residue (source G) and from the combustion of liquid wastes (source H). (Secondary emissions occur when VOC are emitted with the combustion flue gas.)

## A.4 Vinylidene Chloride Process

Methyl chloroform is produced by reacting vinylidene chloride and hydrogen chloride in the presence of a catalyst ($FeCl_3$). This hydrochlorination of vinylidene chloride to methyl chloroform takes place according to the following reaction:

$$CH_2{=}CCl_2 \quad + \quad HCl \xrightarrow{FeCl_3} CH_3CCl_3$$

| | | |
|---|---|---|
| Vinylidene chloride | Hydrogen chloride | Methyl chloroform |

The vinylidene chloride used as raw material is obtained by: (a) chlorination of ethylene or 1,2-dichloroethane with chlorine to form 1,1,2-trichloroethane and by-product hydrogen chloride; and (b) dehydrochlorination of the 1,1,2-trichloroethane to form vinylidene chloride. The reaction of vinylidene chloride with the hydrogen chloride evolved in step (a) yields methyl chloroform (Lowenheim and Moran, 1975).

Presently, the vinylidene chloride process is used to produce methyl chloroform only when the demand exceeds PPG's new plant capacity (Section 2.4.1). The new plant uses vinyl chloride as the primary raw material. Since the vinylidene chloride process is effectively on standby, there was little information given in the Hydroscience report (Hydroscience, 1979) and only a cursory overview of the process presented in the MRI report (EPA, 1979a).

Figure A-3 represents a "derived" flow diagram for the vinylidene chloride process.

Vinylidene chloride and hydrogen chloride from storage and recycled gases from the first distillation column (primarily methyl chloroform, vinylidene chloride and hydrogen chloride) are fed to the hydrochlorination reactor. The reaction of vinylidene chloride with hydrogen chloride is ideally conducted in the liquid phase with ferric chloride as a catalyst. The chemical reaction is conducted at 25 to 35° C under slightly superatmospheric pressure.

Ammonia is added to the hydrochlorination reactor effluent, forming a solid complex with the residual hydrogen chloride and the ferric chloride catalyst. The complex is removed by the spent catalyst filter as a semisolid waste stream (source G). The filtered hydrocarbon stream passes to the distillation column where lower boiling point compounds; mostly unreacted hydrogen chloride and vinylidene chloride; are removed overhead for recycle.

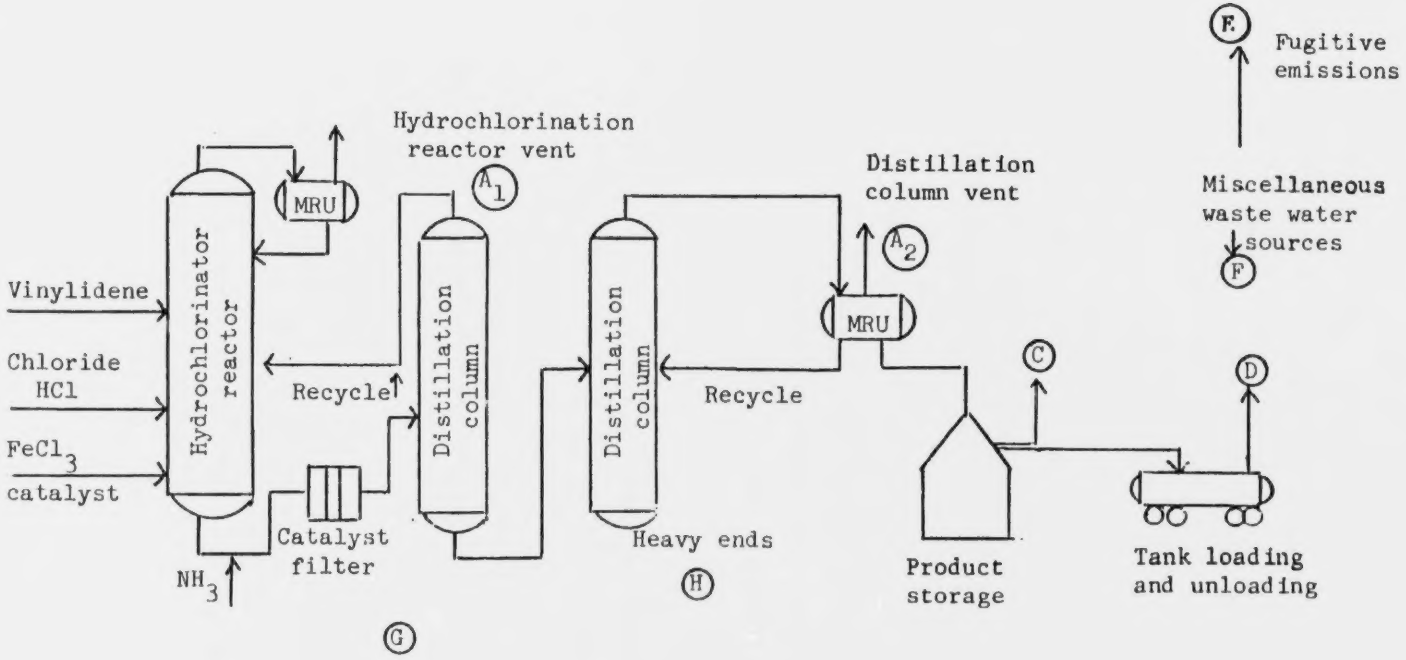

Vinylidene
Chloride
HCl
FeCl3
catalyst
Hydrochlorinator reactor
MRU
NH3
Catalyst filter
Recycle
Hydrochlorination reactor vent
A1
G
Distillation column
Distillation column
Heavy ends
H
Recycle
Distillation column vent
A2
MRU
C
Product storage
D
Tank loading and unloading
E
Fugitive emissions
Miscellaneous waste water sources
F

Figure A-3 Derived Flow Diagram of the Production Process from Vinylidene Chloride

Crude methyl chloroform is removed as a bottom stream for further purification in the second distillation column. The second column removes high-boiling point chlorinated organics (tars) as a waste stream (source H) from the bottom. The overhead stream, composed of methyl chloroform, is condensed by a mechanical refrigeration unit (MRU). Liquid methyl chloroform is transferred from the MRU to product storage.

The hydrochlorination reactor distillation column vents ($A_1$ and $A_2$), which release primarily noncondensable gases, are sources of process emissions. Storage emissions (vent C) include emissions from methyl chloroform product storage. Handling emissions (source D) result from the loading of methyl chloroform into tank trucks or tank cars for shipment.

Fugitive emissions (E) occur when leaks develop in valves or compressor seals. When process pressures are higher than the cooling-water pressure, volatile organic compounds (VOC) can leak into the cooling water and escape as a fugitive emission from the cooling towers.

Secondary emissions can occur when wastewater from miscellaneous process sources (source F) is sent to a wastewater treatment system and the contained VOC are desorbed. Other sources of secondary emissions are from the combustion of catalyst residue (source G) and organic wastes (source H). These emissions occur when VOC are emitted with the combustion flue gas.

# APPENDIX B

## Legislation Effecting the Use of Methyl Chloroform

Methyl chloroform is used in several non-consumptive applications which favor the use of chlorinated solvents. The status of methyl chloroform as a solvent for various end-uses is changing as a result of OSHA regulations and existing or potential regulations concerning ozone formation in the troposphere and ozone depletion in the stratosphere.

Rule 66, the well known Los Angeles Ordinance that was designed to reduce photochemical oxidation, has led to widespread solvent substitution in the metal cleaning industry. Methyl chloroform, an exempt solvent, has been widely substituted for trichloroethylene, a non-exempt solvent. Rule 66 was originated in 1966 and many other locations subsequently enacted similar ordinances. Regulations under Rule 66 are stringent controlling emissions to 18 kg/day. Given the alternative of trying to meet the regulations or substituting with an exempt solvent, the decision in the metal cleaning industry has invariably been to substitute.

In other industrial applications however, where chlorinated solvents can be substituted by water, or other solvents, the trend has been to phase out the use of cholorinated solvents.

Under the Clean Air Act Amendment, EPA is given the authority to pass legislation to regulate depletion of ozone in the stratosphere as well as formation of ozone in the troposhere. The primary strategy used to attain ozone standards in the troposphere is to control emissions of volatile organic chemicals under the State Implementation Plans (SIP's). Many SIP's currently being prepared exempt methyl chloroform while requiring RACT (Reasonable Available Control Technology) for trichloroethylene. Methyl chloroform was originally exempt because it is resistant to tropospheric hydrolysis and does not lead to ozone formation in the troposphere. However, evidence that the long half-life of methyl chloroform permits diffusion of this compound into the stratosphere and subsequent destruction of stratospheric ozone, has led EPA to consider regulating methyl chloroform under Section III of the Clean [illegible] Act. Under this section, methyl chloroform could be regulated as a solvent in the metal cleaning industry under standards of performance for New Stationary Sources. Although, EPA is considering the deletion of methyl chloroform from the list of exempt solvents, they are not necessarily going to disapprove SIP's that have exempted this solvent, since many states have nearly completed preparation of their regulatory package (Kellum, EPA, 1979c).

In the uncertainty surrounding regulations of methyl chloroform, certain industries have begun to phase out the use of this solvent as well as other chlorinated solvents. For instance, researchers in the adhesives industry are concentrating their efforts on developing water based adhesives and hot metals, rather than investigating new applications for exempt solvents. Many of the adhesives industries indicated that they are phasing out use of chlorinated solvents (UPACO, 1979; Mobay, 1979; Hercules, 1979), although they are still very important in rubber based cements.

Similar sentiment was expressed by contacts in the leather tanning and textile industries. Existing and future OSHA regulations under the Clean Air Act Amendments have encouraged these industries to phase out the use of chlorinated solvents.

# APPENDIX C-1

## BACKGROUND

Solvent degreasing describes those processes which use non-aqueous solvents to clean and remove soils from metals. Based on a 1972 Census of Manufacturers the metal working industry includes the eight SIC categories listed in Table C-1.

TABLE C-1 USE OF SOLVENT DEGREASING AMONG METAL WORKING SIC CATEGORIES

| | SIC Category | Percent Using Solvent Degreasing | Percent Using Solvent Degreasing & Alkaline Wash |
|---|---|---|---|
| Metal Furniture | 25 | 29 | 17 |
| Primary Metals | 33 | 17 | 19 |
| Fabricated Products | 34 | 23 | 19 |
| Non-Electric Mach. | 35 | 33 | 19 |
| Electric Equipment | 36 | 33 | 22 |
| Transportation Equip. | 37 | 22 | 28 |
| Instruments/Clocks | 38 | 42 | 23 |
| Misc. | - | 30 | 8 |
| TOTAL | - | 28 | 20 |

(Source: Dow. 1976)

There are approximately 184,000 plants within these industrial categories (D&B, 1977 and Census Manufacturers, 1979). The percentage of metal working operations using solvent degreasing has been estimated by two independent surveys at 24 percent and 29 percent (Dresser, K., 1979; Dow 1976; respectively).

The number of metal cleaning operations was calculated as follows:

$$184{,}000 \text{ plants } \times \frac{24\% + 29\%}{2} = 49{,}000 \text{ plants.}$$

The uncertainty of this number is ±9%.

It is assumed that the plants which practice solvent degreasing are geographically distributed in a pattern that is similar to entire metal working industry. Figure 3.1-1 in the text, shows the geographic distribution of metal working operations.

For purposes of quantifying emissions from solvent degreasing, the following operations are distinquished:

- Wiping - Solvent dampened clothes are used to clean metal parts. Chlorinated solvents are rarely used in these applications.
- Cold Cleaning - Metal parts are cleaned in a tank of solvent maintained at a temperature below the solvent boiling point. There were an estimated 1.35 million cold cleaning operations nationwide in 1978 (CEH, 1978). This represents an increase of 3 percent per year since 1974 when 1.22 million units were reported (EPA, 1977b).
- Open Top Vapor Degreasing - A batch load operation using heated solvent in which the units are loaded continuously by means of a conveyor. The solvent is heated to the boiling point thus creating a zone of solvent vapor contained by a set of cooling coils.

  At the close of 1978 there were 32,000 open top vapor degreasers (CEH, 1978). A separate report estimated 22,000 units in 1974 (EPA, 1977b) suggesting a 10 percent growth rate per year.
- Conveyorized Vapor Degreasing - Parts are loaded continuously by means of a conveyor. These units can operate in either the cold cleaning or vapor degreasing mode. 5,000 conveyorized degreasers were reported in 1978 (CEH, 1978).

## APPENDIX C-2 -- CALCULATION TO DETERMINED PERCENTAGE OF METHYL CHLOROFORM USED IN COLD CLEANING AND VAPOR DEGREASING

Estimate of Quantities of Methyl Chloroform Reported by Metal Cleaners Survey by Dow in 1974

(Representative of segment surveyed only)

| | Source |
|---|---|
| 1) Total methyl chloroform accounted for in survey:<br>30,600 kkg (cold cleaning) + 53,900 kkg (vapor degreasing) = 84,500 kkg used metal cleaning | Dow, 1976 |
| 2) Percent used in cold cleaning:<br>30,600 kkg/84,500 kkg = 36 percent | Dow, 1976 |
| 3) Percent used in solvent degreasing:<br>53,900 kkg/84,500 kkg = 64 percent | Dow, 1976 |

### Solvent Substitution

4) Solvent substitution of trichloroethylene in cold cleaning since 1974 is estimated by multiplying the total used in cold cleaning in 1974 times total 1978 production divided by total 1974 production, and subtracting this quantity from the amount of trichloroethylene used in cold cleaning in 1974.

$$19{,}600 \times \frac{300 \text{ kkg produced 1978}}{388 \text{ kkg produced 1974}} = 15{,}500 \text{ kkg trichloroethylene}$$

19,600 kkg - 15,500 kkg trichloroethylene = 4,100 kkg substituted by methyl chloroform

5) Solvent substitution of trichloroethylene in vapor degreasing.

$$50{,}700 \text{ kkg} \times \frac{300 \text{ kkg produced 1974}}{380 \text{ kkg produced 1978}} = 40{,}000 \text{ kkg trichloroethylene still used}$$

50,700 kkg - 40,000 kkg = 10,700 kkg substituted by methyl chloroform

6) Accounting for solvent substitution in cold cleaning.

30,600 kkg + 4,100 kkg = 34,700 kkg

7) Accounting for solvent substitution in vapor degreasing.

53,900 kkg + 10,700 kkg = 64,600 kkg

### Annual Growth Rate

8) 3 percent growth rate was estimated for cold cleaning operations based on number of units reported in 1974 $(1.22 \times 10^6)$ and number reported in 1978 $(1.35 \times 10^6)$

Source
EPA, 1977b
SRI, 1978

$\therefore$ 34,700 kkg in 1974 x $(1.03)^4$ = 39,055 kkg in 1978

9) 10 percent annual growth rate was estimated for vapor degreasing operations based on number of units reported in 1974 (22,000) and the number reported in 1978 (32,000)

64,600 kkg in 1974 x $(1.10)^4$ = 95,200 kkg in 1978

10) Total quantity of methyl chloroform = 134,200 kkg = 40,200 kkg + 94,000 kkg

### Total Percent of Methyl Chloroform for Industry Segment Surveyed in 1978

11) Percent used in cold cleaning = Total quantity used divided by quantity used in cold cleaning

40,200 kkg/134,200 kkg = 30 percent

12) Percent used in vapor degreasing = Total quantity used divided by quantity used in vapor degreasing.

94,000 kkg/134,200 kkg = 70 percent

## APPENDIX C-3

## METHYL CHLOROFORM RELEASES FROM COLD CLEANING

### Total Cold Cleaners Using Methyl Chloroform

The following assumptions are used to estimate the number of cold cleaners using methyl chloroform:

| | | Source |
|---|---|---|
| 1) | $1.35 \times 10^6$ cold cleaning units | (SRI, 1978) |
| 2) | 30 percent of total are manufacturing units which are more likely to use chlorinated solvents | (EPA, 1977b) |
| 3) | 18 percent of manufacturing units use methyl chloroform | Based on Dow Survey (1976) and corrected to account for solvent substitution |

| Total Cold Cleaning Units | Percent Using are Manufacturing Units | Percent Using Methyl Chloroform | = | Cold Cleaners Using Methyl Chloroform |
|---|---|---|---|---|
| $(1.35 \times 10^6)$ | (0.3) | (0.18) | = | 72,900 units |

The estimated uncertainty for the number of cold cleaning operations using methyl chloroform is ±20%.

### Losses from Non-Boiling Conveyorized Degreasers

Losses of methyl chloroform from non-boiling conveyorized degreasers are considered in section 3.1.2.4. Losses from these units are subtracted from the total cold cleaning units.

It is estimated that there are 5000 conveyorized degreasers (±10%), 15 percent (±27%) of which are non-boiling conveyorized degreasers (SRI, 1978; EPA, 1977b). Using the results of the Dow Survey and accounting for solvent substitution for trichloroethylene, it is estimated that about 18 percent (±30%) of the cold cleaners use methyl chloroform. The number of conveyorized non-boiling degreasers using methyl chloroform is estimated as follows:

| Number of Conveyorized Units | Percent which are Non-boiling Conveyorized Degreasers | Percent Using Methyl Chloroform | = | Total Number of Non-boiling Conveyorized Degreasers Using Methyl Chloroform |
|---|---|---|---|---|
| (5,000) | (0.15) | (0.30) | = | 225 units |

The accuracy of the number of non-boiling conveyorized degreasers is ±42%.

Average loss for a non-boiling conveyorized degreaser has been estimated at 47 kkg/yr (±10%) (EPA, 1977b) and total methyl chloroform losses from these units are estimated using the following equation:

| Methyl Chloroform Losses per Unit | Number of Units | = | Total Methyl Chloroform Losses from Non-boiling Conveyorized Degreasers |
|---|---|---|---|
| (47 kkg/unit) | (225) | = | 10,600 kkg/yr |

Total methyl chloroform losses from non-boiling conveyorized degreasers has an uncertainty of ±43%.

The losses from non-boiling conveyorized degreasers are subtracted from total cold cleaning losses (56,300 kkg, +39%, -2%) to estimate the losses from non-conveyorized cold cleaners.

$$56{,}300\text{ kkg} - 10{,}600\text{ kkg} = 45{,}700\text{ kkg}$$

The estimated uncertainty is +39%, -2%.

The average loss per non-conveyorized unit can then be estimated as follows

$$\frac{\text{Total Methyl Chloroform Losses from Non Conveyorized Cleaners}}{\text{Total No. of Cold Cleaning Units}} = \text{Methyl Chloroform Losses per Non-conveyorized Cold Cleaner}$$

$$\frac{(45{,}700\text{ kkg})}{(72{,}900\text{ units})} = 0.63\text{ kkg/unit}$$

The uncertainty is estimated to be +44%, -20%.

# APPENDIX C-4 CALCULATIONS FOR ENVIRONMENTAL LOSSES OF METHYL CHLOROFORM FROM COLD CLEANING

This appendix estimates multimedia environmental releases of methyl chloroform from the use of non-conveyorized cold cleaners.

## Waste Solvent

OAQPS estimated that 40-60 percent of the virgin solvent becomes waste solvent in a typical manufacturing cold cleaner (EPA, 1977b). However, most cold cleaners did not recycle at that time and it was assumed that about 50 percent of losses are waste solvent in operations which are not reclaiming solvent.

An estimate for the number of cold cleaners which are currently recycling methyl chloroform is difficult to obtain. JRB estimates that about 30 percent (±33%) of the cold cleaners are recycling the waste solvent. This estimate is based on conversations with Dow and the National Solid Waste Management Association (NSWMA); it was estimated that at the time of the Dow Survey about 20 percent of the operations were reclaiming methyl chloroform but there is a trend towards increased recycling (Richards, D., 1979; Dow, 1976; NSWMA, 1979).

An Effluent Guidelines survey conducted for the Mechanical Products Industries found that 73 percent of solvents were either reclaimed or contract hauled for reclamation in 1978. However, this survey did not distinguish between cold cleaners and vapor degreasers (Dresser, K., 1979).

OAQPS estimated that 45 percent of all metal cleaning solvents were recycled in 1974 and that most of the recycled solvents were halogenated (EPA, 1977b).

Assuming that waste solvent was 50 percent (+10%, -25%) of the solvent is lost, the average waste solvent per unit can be estimated as follows:

| Total Methyl Chloroform Losses per Unit per Year | Percent Waste Solvent | = | Average Unit Losses of Waste Solvent |
|---|---|---|---|
| (0.63 kkg/unit) | (0.5) | = | 0.315 kkg/unit |

For cold cleaning units with solvent recovery at 90 percent efficiency (+7%, -2%), the average waste solvent losses are estimated as follows:

| Average Losses of Waste Solvent per Unit | 1-Efficiency of Solvent Recovery | = | Average Waste Solvent Losses from Solvent Recovery |
|---|---|---|---|
| (0.315 kkg/unit) | (1.0-0.9) | = | 0.0315 kkg/ unit |

Total annual losses from waste solvent are estimated by multiplying the average loss per unit by the number of units.

| Average Waste Solvent per Unit Without Solvent Recovery | Total Number of Cold Cleaning Units | Percent Which do not Recover Solvent | = | Total Waste Solvent from Units Without Solvent Recovery |
|---|---|---|---|---|
| (0.315 kkg/unit) | (72,900 units) | (0.7) | = | 16,100 kkg |

| Average Waste Solvent per Unit After Solvent Recovery | Total Number of Cold Cleaning Units | Percent Which Recover Waste Solvent | = | Total Waste Solvent Where Recovery is Practiced |
|---|---|---|---|---|
| (0.0315 kkg/unit) | (72,900 units) | (0.3) | = | 689 kkg |

Because of the uncertainty related to waste reclamation practices, our estimate for the quantities of still bottoms generated is not considered more accurate than +56%, -73%. Our estimate for the quantity of waste solvent generated from units without solvent recovery is probably accurate to +43%, -29%.

## Waste Solvent Disposal

The results of the 1974 Dow Survey suggested that unreclaimed waste was handled as follows:

- o 3 percent (±5%) was incinerated at 95 percent efficiency (±4%)
- o 44 percent (+15%, -5%) was landfilled
- o 53 percent (+5%, -15%) was flushed.

More recent information was sought to update the trends on the final disposal of waste solvent, but information on current practices was not consistent with regards to landfilling and flushing. A major manufacturer of solvent degreasing equipment indicated that most of their clients disposed of waste solvent by landfilling, but that flushing was also common. Incineration was not widely practiced. (Personal Communication, 1979).

An Effluent Guidelines survey (1979) found that a large majority of waste solvent was flushed; 79 percent of plants did not reclaim and discharged to municipal sewers; 21 percent discharged to land; and none incinerated (only 14 plants reporting). Based on these contacts, it was decided to use the results of the Dow Survey and to use an estimated uncertainty of +5%, -15% and +15%, -5% for waste disposal to water and land and ±5% for the quantity incinerated. The quantities disposed of to various media can be estimated as follows:

| Total Waste Solvent Generated | Percent Disposed of to Land, or Water, or by Incineration | = | Quantity Released to Land, or Water, or by Incineration |
|---|---|---|---|
| Land: | | | |
| (16,100 kkg) | (0.44) | = | 7080 kkg landfilled |
| Water: | | | |
| (16,100 kkg) | (0.53) | = | 8530 kkg flushed |

Incinerated:

Assumed 95 percent efficiency for incineration (±4%).

(16,100 kkg) (0.03) (0.95) = 459 kkg incinerated

(16,100 kkg) (0.03) (1-.95) = 24.2 kkg released to air from incineration

Table C-2 summarizes the individual and overall uncertainties for the above derived values.

Table C-2 - Summary of Uncertainties for Waste Solvent

| Waste | Quantity (kkg) | Individual Uncertainty (%) | Overall Uncertainty (%) |
|---|---|---|---|
| Waste Solvent | 16,100 | -- | +43/-29 |
| Releasted to Water | 8,530 | +5/-15 | +43/-33 |
| Landfilled | 7,080 | +15/-5 | +46/-29 |
| Incinerated | 459 | ±5/±4 | +43/-30 |
| Released to Air from Incineration | 24.2 | ±80 | +91/-85 |

Disposal of Still Bottoms:

It was estimated that 689 kkg (+56%, -73%) of methyl chloroform waste solvent is generated from solvent recovery. Little information was available on the final disposal of the waste solvent. Some solvent reclamation services incinerate the waste solvent (Solvent Recovery Service of the Northeast, 1979) although there are still few approved incinerators in the country (NSWMA, 1979). JRB assumed that 25 percent (±30%) of these still bottoms are incinerated at 95 percent efficiency (±4%) and the remaining 75 percent (±9%) are landfilled. The quantities incinerated, emitted to air from incineration or landfilled are estimated as follows:

Incinerated

(689 kkg) (0.25) (0.95) = 164 kkg

Emitted to air from incineration

(689 kkg) (0.25) (1-0.95) = 8.61 kkg

Landfilled

(689 kkg) (0.75) = 517 kkg

The uncertainties of these estimates are +57% and -74% for the quantity landfilled and +102%, -100% from incineration. These uncertainties account for an uncertainty of +56%, -73% for the total still bottoms generated (689 kkg) and ±30% for the percent incinerated as well as an uncertainty of +39 and -2% for the total solvent used in cold cleaning.

### Atmospheric Losses:

Atmospheric losses of methyl chloroform are estimated by subtracting the waste solvent losses from the total solvent losses due to cold cleaning.

| | | | | |
|---|---|---|---|---|
| Total Methyl Chloroform Losses from Non-conveyorized Cold Cleaning | - | Waste Solvent Losses | = | Total Solvent Emitted to Air |
| (45,700 kkg) | - | (16,100 + 689) | = | 28,900 kkg |

The uncertainty of the methyl chloroform emitted to the air from non-conveyorized cold cleaning is +58%, -29%.

Only about 1.5 percent (±50%) of the cold cleaners use carbon adsorption for recovery of atmospheric emissions (Dow, 1976; Raquat, D., 1979). The efficiency for carbon adsorption is about 60 percent (±10%) (Dow, 1976). The remaining solvent is emitted directly into the air. To estimate the quantities of methyl chloroform emitted to the air, the following expressions are used:

| Total Solvent Emitted to Air | Percent of Operations Using Carbon Adsorption | Percent Efficiency of Carbon Adsorption | = | Total Quantity Adsorbed by Carbon |
|---|---|---|---|---|
| (28,900 kkg) | (0.015) | (0.6) | = | 260 kkg |

Assumimg that carbon regeneration is 95 percent effective (±4%) and 95 percent (±4%) of the total methyl chloroform adsorbed will be destroyed during regeneration, the quantities of methyl chloroform destroyed and emitted are calculated as follows:

| Total Methyl Chloroform Absorbed | Percent Regeneration Efficency | = | Methyl Chloroform Destroyed During Regeneration |
|---|---|---|---|
| (260 kkg) | (0.95) | = | 247 kkg |

| Total Methyl Chloroform Adsorbed | 1-Percent Destroyed | = | Methyl Chloroform Emitted to Air from Regeneration |
|---|---|---|---|
| (260 kkg) | (1-0.95) | = | 13.0 kkg |

The overall uncertainties for the quantities adsorbed during carbon adsorption and for the quantity emitted to air from generation are +77%, -59% and +111%, -99% respectively.

The total chloroform emitted directly to the air is determined by subtracting the quantity of methyl chloroform adsorbed to carbon from the total methyl chloroform emitted to air.

(28,900 kkg) - (260 kkg) = 28,600 kkg

Direct air emissions are thought to be accurate to +58% and -29%. Since atmospheric losses were estimated to be the difference between total solvent losses and waste solvent, the uncertainty factor accounts for variations in waste solvent control practices, which in turn would affect atmospheric losses.

## APPENDIX C-5 CALCULATIONS FOR ANNUAL LOSSES OF METHYL CHLOROFORM FROM OPEN TOP VAPOR DEGREASERS (OTVD)

### Average Annual Emissions

It has been estimated that there were about 32,000 (±10%) open top vapor degreasers in operation during 1978 (SRI, 1978). Using the Dow Survey and accounting for solvent substitution, an estimated 30 percent (+15%, -10%) of these units use methyl chloroform (Dow, 1976). The total annual losses from open top vapor degreasers is estimated by subtracting losses from conveyorized vapor degreasers (see Appendix C-6) from the total vapor degreasing losses estimated in Section 3.1.1.

$$\text{Total Vapor Degreasing Losses} - \text{Losses from Conveyorized Vapor Degreasers} = \text{Total Losses from Open Top Vapor Degreasers (OTVD)}$$

$$131{,}000\ \text{kkg} - 39{,}300\ \text{kkg} = 91{,}700\ \text{kkg}$$

The average annual emissions per unit are estimated by dividing the total methyl chloroform released by the number of open top vapor degreasers using methyl chloroform.

$$\frac{\text{Total Methyl Chloroform Released from OTVD}}{\text{OTVD Using Methyl Chloroform}} = \text{Average Annual Emissions Per Unit}$$

$$\frac{(91{,}700\ \text{kkg})}{(32{,}000\ \text{units} \times 0.30)} = 9.55\ \text{kkg/unit}$$

This estimate agress closely ( $<$ 0.5% error) with an estimate of 9.5 kkg made by OAQPS for average unit losses from uncontrolled OTVD (EPA, 1977b). Although the calculated uncertainty for this emission rate is +39%, -42%, we are assuming the square of this uncertainty (+15%, -17%) to account for the similarity between the JRB estimate and the OAQPS estimate.

### Waste Solvent Losses

It has been estimated that 20-25 percent (or 22.5 percent, ±11%) of the total virgin solvent becomes waste solvent (EPA, 1977b). We assume that 75 percent of all OTVD are equipped with stills. This estimate is based on a conversation with Phillips Corporation, a manufacturer of metal cleaning equipment, (Raquat, D., 1979). Similarly, an Effluent Guidelines survey found that 73 percent of the respondents reclaimed solvent (Effluent Guidelines, 1979). Total waste solvent generated is estimated using the following equation:

| Total Methyl Chloroform Losses | Percent of Losses Which are Waste Solvent | = | Total Waste Solvent Generated from OTVD |
|---|---|---|---|
| (91,700 kkg) | (0.225) | = | 20,600 kkg |

Assuming that 75 percent (±10%) of the operations practice solvent recovery at 90 percent efficiency (+7%, -2%), the quantities of still bottoms and unreclaimed waste solvent are estimated using the following series of equations:

| Total Number of OTVD | Percent Which Recover Solvent | = | Total Number of OTVD Practicing Solvent Recovery |
|---|---|---|---|
| (9,600 units)* | (0.75) | = | 7,200 units |

| Total Number of OTVD | Percent Which do not Recover Solvent | = | Total Number of OTVD Which do not Recover Solvent |
|---|---|---|---|
| (9,600 units) | (0.25) | = | 2,400 units |

At those operations which reclaim solvent, only 10 percent (+20%, -70%) of the solvent becomes waste solvent. The average unit losses can be estimated as follows:

| No. of OTVD Which Reclaim Solvent | Percent of Solvent in Still Bottoms | Quantity of Waste Solvent Generated/ Unit | + | No. of OTVD Which do not Reclaim Solvent | Quantity of Waste Solvent Generated/Unit | = |
|---|---|---|---|---|---|---|
| (7,200 units) | (0.1) | (x) | + | (2,400) | (x) | = |

Total Waste Solvent Losses

20,600 kkg

* 32,000 units x 30 percent

x = 6.60 kkg Unreclaimed Waste Solvent/Unit
.1x = 0.660 kkg Still Bottoms/Unit

The total unreclaimed waste solvent is equivalent to the average unit loss times the number of units which do not reclaim solvent.

2,400 units x 6.60 kkg/unit = 15,800 kkg unreclaimed waste solvent.

The total still bottoms are similarly estimated by multiplying the total number of units which reclaim solvent by the average quantity of still bottoms per unit.

7,200 units x 0.660 kkg/unit = 4750 kkg still bottoms

Because of the uncertainty related to solvent recovery practices, our estimate for the quantity of still bottoms generated is only accurate to +29%, -72%. The estimate of 15,800 kkg waste solvent is considered accurate to +36%, -33%.

## Disposal of Still Bottoms

As was the case for cold cleaning operations, we assume that 75 percent (+7%, -3%) of the solvent is landfilled and 25 percent (+10%, -20%) is incinerated at 95 percent efficiency (±4%).

Landfilled:

(4750 kkg) (0.75) = 3560 kkg

Incinerated:

(4750 kkg) (0.25) (0.95) = 1130 kkg

Emitted to air from incineration:

(4750 kkg) (0.25) (1-0.95) = 59.4 kkg

The uncertainties of the quantity of methyl chloroform disposed in landfills, destroyed by incineration, and emitted to the air from incineration are +30%, -72%; +31%, -75%; and +86%, -100% respectively.

## Waste Solvent Disposal

It is assumed that unreclaimed waste solvent is disposed of as follows:

- 3 percent (±5%) is incinerated at 95 percent efficiency (±4%)
- 44 percent (+15%, -5%) is landfilled
- 53 percent (+5%, -15%) is flushed

These estimates are based on the results of the Dow Survey (Dow, 1976). Other information pertaining to the final disposal of waste solvent was discussed in Appendix C-4. The total quantities of unreclaimed solvent disposed of to various media are estimated using the expression:

| Total Waste Solvent | Percent Disposed of to Land, Water or Incinerated | = | Total Solvent to Land, Water or Incinerated |
|---|---|---|---|
| **Incinerated:** | | | |
| (15,800 kkg) | (0.03) (0.95) | = | 450 kkg |
| **Emitted to Air from Incineration** | | | |
| (15,800 kkg) | (0.03) (1-0.95) | = | 23.7 kkg |
| **Landfilled:** | | | |
| (15,800 kkg) | (0.44) | = | 6950 kkg |
| **Flushed:** | | | |
| (15,800 kkg) | (0.53) | = | 8470 kkg |

Table C-4 summarizes the uncertainties of quantities of waste solvent.

Table C-3 Summary of Uncertainties for Waste Solvent from Vapor Degreasing (OTVD)

| Waste | Quantity | Individual Uncertainty % | Overall Uncertainty % |
|---|---|---|---|
| Total waste solvent | 15,800 | -- | +19/-14 |
| Released to water | 8,470 | +5/-15 | +20/-21 |
| Landfilled | 6,950 | +15/-5 | +24/-15 |
| Incinerated | 450 | ±5/±4 | +20/-15 |
| Emitted to air from incineration | 23.7 | ±80 | +82/-81 |

## Direct Atmospheric Losses

Direct atmospheric losses of methyl chloroform are those emissions resulting from diffusion and convection, roof vent emissions and carry out. These losses are equivalent to the total methyl chloroform losses minus losses from waste solvent.

| Total Methyl Chloroform Losses | | Waste Solvent Losses | | Total Direct Atmospheric Emissions |
|---|---|---|---|---|
| (91,700 kkg) | - | (15,800 kkg + 4750 kkg) | = | 71,200 kkg |

Approximately 1.5 percent (±50%) of the OTVD use carbon adsorption systems which operate at about 60 percent (±10%) efficiency (Dow, 1979; Raquat, D., 1979). The quantity of chloroform adsorbed is estimated by multiplying total atmospheric losses by the percent of units using carbon adsorption by the efficiency of recovery.

$$(71{,}200 \text{ kkg})\ (0.015)\ (0.6) = 641 \text{ kkg}$$

It is further assumed that carbon is regenerated at 95 percent efficiency (±4%) and 95 percent (±4%) of the methyl chloroform is destroyed.

| Methyl Chloroform Adsorbed by Carbon | Efficiency of Regeneration | | Quantity of Methyl Chloroform Destroyed in Regeneration |
|---|---|---|---|
| (641 kkg) | (0.95) | = | 609 kkg |

| Total Methyl Chloroform Adsorbed by Carbon | 1-Efficiency of Regeneration | = | Methyl Chloroform Emitted to Air from Carbon Regeneration |
|---|---|---|---|
| (641 kkg) | (0.05) | = | 32.1 kkg |

*Direct atmospheric losses* are equal to the total atmospheric emissions minus the quantity adsorbed by carbon.

(71,200 kkg) - (641 kkg) = 70,500 kkg

Direct atmospheric emissions are considered accurate to +42%, -41%. Since atmospheric losses were estimated as the difference between total solvent losses and waste solvent, the uncertainty factor accounts for uncertainties related to waste solvent control practices and the uncertainty related to total solvent used in vapor degreasing.

The quantities of methyl chloroform destroyed during carbon regeneration and the quantity emitted to air from carbon regeneration are considered accurate to +66%, -65% and +104%, -100%, respectively.

# APPENDIX C-6

## ANNUAL METHYL CHLOROFORM LOSSES FROM CONVEYORIZED VAPOR DEGREASERS

Of an estimated 5,000 conveyorized degreasers (±10%), approximately 85 percent (±5%) of are vaporized degreasers (EPA, 1977b). The percent of conveyorized vapor degreasers (CVD) using methyl chloroform is estimated to be about 30 percent (+15%, -10%) (Dow, 1976). Using these estimates, the total number of CVD using methyl chloroform is determined as follows:

| Total Number of Conveyorized Degreasers | Percent CVD | Percent Using Methyl Chloroform | = | Total No. of CVD Using Methyl Chloroform |
|---|---|---|---|---|
| (5000 units) | (0.85) | (0.3) | = | 1280 units |

OAQPS estimates that 30 percent (±33%) of all solvent losses from vapor degreasers are from CVD. Then, total methyl chloroform losses from these units are estimated as follows:

| Total Methyl Chloroform Losses from Vapor Degreasing | Percent Due to CVD | = | Total Losses from CVD |
|---|---|---|---|
| (131,400 kkg) | (0.3) | = | 39,300 kkg |

This corresponds to an annual average loss of 30.7 kkg/unit (+40%, -42%), which is nearly 30 percent higher than an estimate (23.7 kkg/unit) made by OAQPS for average losses of all solvents (EPA, 1977b). The OAQPS estimate is within the uncertainty given for the calculated average annual loss.

### Waste Solvent

It has been estimated that 10 to 20 percent of the virgin solvent becomes waste solvent from the operation of a CVD (EPA, 1977b). Assuming an average of 15 percent waste solvent (±33%), the quantity of waste solvent generated is determined as follows:

(39,300 kkg) (0.15) = 5900 kkg

Solvent recovery is widely practiced among CVD users with an estimated 85 percent (±10%) of the operations recovering solvents (EPA, 1977b). In order to estimate the quantity of waste solvent in still bottoms and the quantity in unreclaimed waste solvent the following approach is used:

| | | | |
|---|---|---|---|
| Total No. of CVD | Percent Using Solvent Recovery | = | Number of Units Using Solvent Recovery |
| (1280 units) | (0.85) | = | 1090 units |
| Total No. of CVD | Percent Which Do Not Use Solvent Recovery | = | Number of Units Not Using Solvent Recovery |
| (1280 units) | (0.15) | = | 192 units |

Assuming that solvent recovery is 90 percent efficient (+7%, -2%), the waste solvent losses per unit can be estimated from the following expression:

| | | | | | |
|---|---|---|---|---|---|
| No. of Units Which Practice Solvent Recovery | 1-Solvent Recovery Efficiency | Waste Solvent Generated Per Unit | + | No. of Units Which Do Not Reclaim Solvent | Waste Solvent Generated Per Unit |
| (1,090 units) | (0.1) | (x) | | (192 units) | (x) |

= Total Waste Solvent

= 5,900 kkg

$x$ = 19.6 kkg = unreclaimed waste solvent per unit
$0.1x$ = 1.96 kkg = still bottoms per unit

Total waste solvent in still bottoms is equal to the number of units with solvent recovery times the unit waste solvent losses.

1,090 units x 1.96 kkg/unit = 2,150 kkg

Total unreclaimed waste solvent is similarly estimated by multiplying the number of units which do not recover solvent by the average waste solvent generated per unit.

192 units x 19.7 kkg/unit = 3780 kkg

Due to the uncertainty related to waste solvent control practices and to quantity of solvent which is waste solvent, we estimate the uncertainty of these estimates at +29%, -72% for the quantity of still bottoms and +60%, -59% for the quantity of unreclaimed waste solvent.

## Disposal of Waste Solvent

Unreclaimed waste solvent is assumed to be disposed in a pattern similar to that found by Dow for all solvents (Dow, 1976).

- 3 percent (±5%) is incinerated at 95% efficiency (±4%)
- 44 percent (+15%, -5%) is landfilled
- 53 percent (+5%, -15%) is flushed

The quantities of methyl chloroform disposed of to land, water or incinerated are estimated as follows:

Incinerated:

(3780 kkg) (0.03) (0.95) = 108 kkg

Emitted to air from incineration:

(3780 kkg) (0.03) (1-0.95) = 5.67 kkg

Landfilled:

(3780 kkg) (0.44) = 1660 kkg

Flushed:

(3860 kkg) (0.53) = 2000 kkg

Table C-4 summarizes the uncertainties which have been estimated for releases of waste solvent.

Table C-4 Summary of Uncertainty for Waste Solvent from Conveyorized Vapor Degreasers (CVD)

| Waste | Quantity | Individual Uncertainty (%) | Overall Uncertainty (%) |
|---|---|---|---|
| Total Waste Solvent | 3780 | — | +60/-59 |
| Released to Water | 2000 | +5/-15 | +60/-61 |
| Landfilled | 1660 | +15/-5 | +62/-59 |
| Incinerated | 108 | ±5/±4 | +60/-59 |
| Emitted to Air From Incineration | 5.67 | ±80 | +100/-99 |

Disposal of Still Bottoms:

It is assumed that 25 percent (+10%, -20%) of the still bottoms are incinerated at 95 percent efficiency (±4%) and the remaining 75 percent (+7%, -3%) are landfilled.

Incinerated:

(2150 kkg) (0.25) (0.95) = 511 kkg

Emitted to Air from Incineration:

(2150 kkg) (0.25) (1-0.95) = 26.9 kkg

Landfilled:

(2150 kkg) (0.75) = 1610 kkg

The estimate for the percent emitted to land is considered accurate to +7%, -3%. Accounting for an uncertainty of +29%, -72% for the total still bottoms generated, as well as the uncertainty related to total solvent used in CVD (39,300 kkg; +35%, -39%) these estimates are considered accurate to +31%, -75% for methyl chloroform incinerated, +86%, -100% for air emissions, and +30%, -72% for still bottoms landfilled.

Atmospheric Losses:

Total atmospheric emissions are equivalent to the total methyl chloroform losses from CVD minus the waste solvent losses.

| Total Methyl Chloroform Losses From CVD | - | Waste Solvent Losses | = | Direct Atmospheric Emissions |
|---|---|---|---|---|
| (39,300 kkg) | - | (2150 kkg + 3780 kkg) | = | 33,400 kkg |

Roughly 1.5 percent (±50%) of the operations use carbon adsorption to recover solvents and the efficiency of this operation is about 60 percent (±10%) (Dow, 1976; Raquat, D., 1979).

| Direct Atmospheric Emissions | Percent Using Carbon Adsorption | Percent Efficiency | = | Methyl Chloroform Adsorbed in Carbon Adsorption |
|---|---|---|---|---|
| (33,400) | (0.015) | (0.6) | = | 301 kkg |

It is further assumed that carbon is regenerated at 95 percent efficiency (±4%) and 95 percent (±4%) of the methyl chloroform is destroyed during regeneration. The remaining 5 percent is emitted to air during regeneration.

| Total Methyl Chloroform Adsorbed | Percent Efficiency for Regeneration | = | Quantity Destroyed During Regeneration |
|---|---|---|---|
| (301 kkg) | (0.95) | = | 286 kkg |

| Total Methyl Chloroform Adsorbed | Percent Emitted During Regeneration | = | Quantity Emitted to Air During Regeneration |
|---|---|---|---|
| (301 kkg) | (0.05) | = | 15.1 kkg |

Direct atmospheric losses are equal to the total atmospheric emissions minus the quantity adsorped by carbon adsorption.

$$(33{,}400 \text{ kkg}) - (301 \text{ kkg}) = 33{,}100 \text{ kkg}$$

This estimate for air emissions is considered accurate to +35%, -39%. Since atmospheric releases were determined by subtracting waste solvent losses from total solvent losses. This uncertainty accounts for uncertainties related to waste solvent and total solvent.

The uncertanties for the quantity destroyed during regeneration and for the quantity emitted to air during regeneration are +62%, -64% and +101%, -100%.

## APPENDIX C-7

## LOSSES OF METHYL CHLOROFORM FROM NON-BOILING CONVEYORIZED DEGREASERS

The OAQPS has estimated that there are 5000 conveyorized degreasers (±10%), 15 percent (±27%) of which are Conveyorized Non-Boiling Degreasers (CND). Using the Dow Survey, JRB estimates that 30 percent (+15%, -10%) of the CND use methyl chloroform (Dow, 1976). The total number of CND using methyl chloroform is estimated as follows:

| Total Number of Conveyorized Degreasers | Percent Which Are CND | Percent Using Methyl Chloroform | = | Total Number of CND Using Methyl Chloroform |
|---|---|---|---|---|
| (5000) | (0.15) | (0.30) | = | 225 units |

Total methyl chloroform losses from CND were estimated by assuming an average unit loss of 47 kkg/unit (±10%). This is an estimate made by OAQPS for all solvents and the actual losses of methyl chloroform undoubtedly vary from other solvents (EPA, 1977b).

| Total Number of CND | Average Loss Per Unit | = | Total Methyl Chloroform Losses From CND |
|---|---|---|---|
| (225 units) | (47 kkg/unit) | = | 10,600 kkg |

Waste Solvent

It has been estimated that 10-20 percent of the virgin solvent becomes waste solvent during the operation of a CND (OAQPS, 1977). Assuming an average of 15 percent (±33%) of the solvent becomes waste solvent, the total waste solvent can be estimated using the following expression:

| Total methyl Chloroform Losses | Percent of Waste Solvent | = | Total Waste Solvent |
|---|---|---|---|
| (10,600 kkg) | (0.15) | = | 1590 kkg |

This estimate includes losses from unreclaimed waste solvent as well as from still bottoms and is considered accurate to +47%, -46%.

Assuming, as we did for CVD, that solvent recovery is practiced by 85 percent (±10%) of the operations at 90 percent efficiency (+7%, -2%), we can estimate the quantities which are still bottoms and unreclaimed waste solvent using the following expressions:

| Number of CND | Percent Which Reclaim Solvent | = | Number Which Reclaim Solvent |
|---|---|---|---|
| (225 units) | (0.85) | = | 191 units |

The remaining 35 CND's do not practice solvent recovery. The waste solvent losses for each of these units can be estimated as follows:

| No. of Units With Solvent Recovery | 1- Solvent Recovery Efficiency | Waste Solvent Per Unit | + | No. of Units Without Solvent Recovery | Waste Solvent Per Unit |
|---|---|---|---|---|---|
| (191 units) | (0.1) | (X) | + | (34) | (X) |

= Total Waste Solvent

= 1590 kkg

x = 29.4 kkg unreclaimed waste solvent
0.1x = 2.94 kkg still bottoms

| No. of Units With Solvent Recovery | Quantity Still Bottoms Per Unit | = | Total Quantity Still Bottoms |
|---|---|---|---|
| (191) | (2.94 kkg) | = | 562 kkg |

| No. of Units Without Solvents | Quantity of Unreclaimed Solvent | = | Total Unreclaimed Wasted Solvent |
|---|---|---|---|
| (34) | (29.4 kkg) | = | 1030 kkg |

Our estimate for the quantity of unreclaimed waste solvent is considered accurate to +35%, -32% and the estimate for still bottoms is accurate to +39%, -77%.

### Disposal of Waste Solvent

Unreclaimed waste solvent is assumed to be disposed of as follows:

- 3 percent (±5%) is incinerated at 95 percent efficiency (±4%)
- 44 percent (+15%, -5%) is landfilled
- 53 percent (+5%, -15%) is flushed

| Total Methyl Chloroform Unreclaimed Waste Solvent | Percent Incinerated, Landfilled and Flushed | = | Total Quantity Incinerated, Landfilled or Flushed |
|---|---|---|---|
| Incinerated: | | | |
| (1030 kkg) | (0.03) (0.95) | = | 29.4 kkg |
| Emitted to Air from Incineration: | | | |
| (1030 kkg) | (0.03) (1 -0.95) | = | 1.55 kkg |
| Landfilled: | | | |
| (1030 kkg) | (0.44) | = | 453 kkg |
| Flushed: | | | |
| (1030 kkg) | (0.53) | = | 546 kkg |

Table C-3 summarizes the uncertainties related to release from waste solvent.

Table C-5 Summary of Uncertainties for Solvent from Conveyorized Vapor Degreasers (CND)

| Waste | Quantity | Individual Uncertainty (%) | Overall Uncertainty (%) |
|---|---|---|---|
| Total Waste Solvent | 1030 | -- | +35/-32 |
| Releases to Water | 546 | +5/-15 | ±35 |
| Landfilled | 453 | +15/-5 | +38/-32 |
| Incinerated | 29.4 | ±5/±4 | +36/-33 |
| Released to Air fron Incineration | 1.55 | ±80 | +87/-86 |

Disposal of Still Bottoms:

JRB estimates that 75 percent (+7%, -3%) of the still bottoms are landfilled and 25 percent (+10%, -20%) are incinerated at 95 percent efficiency (±4%).

Methyl Chloroform in Still Bottoms   Percent Landfilled   =   Total Still Bottoms Landfilled

(546 kkg)   (0.75)   =   410 kkg

Methyl Chloroform in Still Bottoms   Percent Incinerated   Efficiency   =   Total Still Bottoms Incinerated

(546 kkg)   (0.25)   (0.95)   =   130 kkg

Methyl Chloroform in Still Bottoms   Percent Incinerated   1-Efficiency   =   Total Emitted to Air from Incineration

(546 kkg)   (0.25)   (1-0.95)   =   6.83 kkg

These still bottoms estimates are considered accurate to the following:

- Landfilled +36%, -35%
- Incinerated +36%, -40%
- Incinerator Air Emission +88%, -90%.

## Direct Atmospheric Emissions

Direct atmospheric emissions are estimated by subtracting the total waste solvent generated from the total methyl chloroform losses from CND.

(10,600 kkg) - (1590kkg) = 9010 kkg

The quantity actually emitted to air is adjusted to account for an estimated 1.5 percent (±50%) of the operations which use carbon adsorption systems operating at about 60 percent efficiency (±10%).

| Total Air Emissions | Percent Units Using Activated Carbon | Percent Efficiency | = | Total Methyl Chloroform Adsorbed By Activated Carbon |
|---|---|---|---|---|
| (9010 kkg) | (0.015) | (0.6) | = | 81.1 kkg |

Activated carbon regeneration is assumed to be 95 percent efficient (±4%). 95 percent (±4%) of the methyl chloroform is assumed to be destroyed during regeneration and the remaining 5 percent (±80%) is assumed to be emitted to air.

| Methyl Chloroform Adsorbed | Efficiency of Regeneration | = | Quantity Destroyed During Regeneration |
|---|---|---|---|
| (81.1 kkg) | (0.95) | = | 77.0 kkg |

| Methyl Chloroform Adsorbed | 1-Efficiency of Regeneration | = | Quantity Emitted To Air from Regeneration |
|---|---|---|---|
| (81.1 kkg) | (1-0.95) | = | 4.06 kkg emitted to air |

The quantities destroyed and emitted to the air during regeneration are accurate to ±69% and +106%, -100%, respectively.

The total actual direct atmospheric losses are estimated to be the difference between the total atmospheric releases and the quantity adsorbed by carbon adsorption.

(9010 kkg) - (81.1 kkg) = 8930 kkg lost to air

Air emissions are considered accurate to +47%, -46%.

## APPENDIX C-8

## GEOGRAPHIC BREAKDOWN FOR METAL CLEANING REGIONS PRESENTED IN SECTION 3.1

In section 3.1, data on metal cleaning is presented with reference to geographic locations. The following lists the states within each location.

### NORTHEAST

Connecticut
Delaware
Maine
Maryland
Massachusetts
New Hampshire
New Jersey
New York
Pennsylvania
Rhode Island
Vermont

### SOUTHEAST

Alabama
Florida
Georgia
No. Carolina
So. Carolina
Tennessee
Virginia
Arkansas
Washington, D.C.
Puerto Rico

### MID-WEST

Illinois
Indiana
Kentucky
Michigan
Ohio
West Virginia
Wisconsin

### FAR WEST

Arizona
California
Hawaii
Idaho
Nevada
Oregon
Washington
Utah

### NORTH CENTRAL

Colorado
Iowa
Kansas
Minnesota
Missouri
Montana
Nebraska
North Dakota
South Dakota
Wyoming

### SOUTHWEST

Louisiana
Mississippi
Oklahoma
Texas
New Mexico

## APPENDIX D-1

### List of Products Containing Methyl Chloroform

| Name of Products | Producers | % of Methyl Chloroform in the Formulation | Purpose of Use |
|---|---|---|---|
| Amway Drain Mate | Amway Corp. | u.k. | Solvent based Drain Cleaner |
| Amway Dri-Fab | Amway Corp. | u.k. | Water Repellant Spray |
| Amway Oven'N'Grill | Amway Corp. | u.k. | Aerosol Over Protectorant |
| Amway Remove | Amway Corp. | u.k. | Spot Remover |
| Amway Wonder Mist | Amway Corp. | u.k. | Aerosol Lubricant |
| Anchor-Weld 0911 | Roberts Consolidated Ind. | - | Safety Solvent |
| Anchor-Weld 2000 | Roberts Consolidated Ind. | - | Safety Brushage Contact Cement |
| Balkampchoke Cleaner | Balkamp, Inc. | 23% | Choke Cleaner |
| Barton's Spot Remover | Dyanshine Products Division | - | Spot Remover |
| Carbo-Cholor | Sunnyside Products Inc. | - | Metal Cleaner,<br>Spot Remover,<br>Grease and tar Remover |
| Carbona No. 10 Special Spot Remover | Carbona Products Co. | 10% | Spot Remover |
| Carbona Spray Spot Remover | Carbona Products Co. | 25% | Aerosol Spot Remover |
| Carter's Type Cleaner | Carter's Ink | - | Ink Cleaner |
| Difficult Stains | Albatross Chemical | - | Cleaning Fluid |
| Dowclene | Dow Chem., U.S.A. | Approx 100% | Spot Remover Aerosol |
| Dressup | Dolge C.B. Co. | - | Furniture Polish |
| Edwal Color Film Cleaner | Edwal Scientific Products Corp. | -<br>- | Photographic Supply |
| Glamorene Spot Clean | Glamorene Products Corp. | - | Aerosol Powder-Spot Cleaner |
| Gripdust | Dolge C.B. Co. | - | - |
| IBM Adhesive | IBM | - | - |
| IBM Cleaning Fluid | IBM | - | - |
| IBM-SMS Card Contact Cleaner | IBM | - | - |
| IBM Stain Remover | IBM | - | - |
| IBM Tape Developer Cleaner | IBM | - | - |

APPENDIX D-1 (cont.)

## List of Products Containing Methyl Chloroform

| Name of Products | Producer | % of Methyl Chloroform in the Formulation | Purpose of Use |
|---|---|---|---|
| Kitchen Drano (Liquid) | Drackett | Approx. 75% by wt. | Drain Cleaner |
| Mildew stop Spray | Cardinal Products Corp. | 25% | Mold-Mildew and Musty Odor Preventative |
| Moxie 50 W.P. | Ansul | 6 % | Insecticide |
| Muffi Spot Remover | Plough | - | Spot Remover |
| OAB 37 | Kentile | - | On and Below Grade Adhesive |
| One Time Rug Frost | One Time Package Prod. | - | Spot Remover |
| P-3576 | Calgon Corp. | - | Solvent |
| Pow Liquid Drain Cleaner | Penn Champ | 99 % | Drain Cleaner |
| Quik'n Easy Spot Lifter | Penn Champ | 70 % | Spot Remover |
| Roberts 41-0911 | Roberts Consolidated Ind. | - | Universal Cuslieon Back Seam Solvent |
| Roberts 41-4001 | Roberts Consolidated Ind. | - | Carpet Pad Adhesive |
| Roberts 41-4015 | Roberts Consolidated Ind. | - | Cushion Back Seam Adhesive |
| Sila-Slide | Scientific International Research Inc. | -<br>- | Multi-Purpose<br>Silicone Lubricant; Industrial Use |

Source: Chemcial Toxicology of Commercial Products, 1976

Appendix D-2 -- Registered Pesticide Containing Methyl Chloroform (cont.)

| Product | Use | Company | Methyl Chloroform |
|---|---|---|---|
| Moorehead 10% DD-VPspray | Tobacco warehouses | Moorehead Ind., Inc.<br>Hopkinton, MA | 20% |
| Moorehead 50% - WE conc. | Tobacco warehouses | Moorehead Ind., Inc.<br>Hopkinton, MA | 30% |
| Swit - wasp & hornet spray | Insecticide | Dymon, Inc.<br>Kansas City, KA | - |
| Anti Shield | | Anti-shield, Inc.<br>Louisville, KY | - |

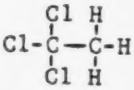
Source: Chemical Toxicology of Commercial Products, 1976

## Appendix D-2 -- Registered Pesticide Containing Methyl Chloroform

| Product | Use | Company | Methyl Chloroform |
|---|---|---|---|
| Dog Shield - Dog Repellant | Personal protection from dog | Chase Products<br>Broadview, IL | - |
| Prentox - 50% DDVP conc. | | Prentice Drug & Chem.<br>N.Y., NY | 30% |
| Prentox - DDVP - aerosol conc. #G-1553 | | Prentice Drug & Chem.<br>N.Y., NY | 64% |
| Prentox - DDVP aerosol conc. | For manufacturing purposes only | Prentice Drug & Chem.<br>N.Y., NY | 67% |
| Capitol DDVP conc. aerosol | | Capitol Chem. Co.<br>Washington, DC | - |
| Fumo - aero-spray | Industrial use only | Fumol Corp.<br>L.I., NY | - |
| Bruce Terminex | Professional insecticide | Terminex Div. of Cook Industries<br>Memphis, TN | 8% |
| Clipper Mate | Lubricates, sanitizers cools | Carson Chem., Inc.<br>New Castle, IN | - |
| Stephenson Chem. - DDVAP 14% | | Stephenson Chem. Co.<br>New Castle, IN | - |
| Stephenson Chem. - DD-VP-20% | | Stephenson Chem Co.<br>New Castle, IN | - |
| Carmel Chem. - non-flammable vapona fogging insecticide | Insecticide | Carmel Chem. Corp.<br>Westfield, IL | 60% |
| Carmel Chem. - non-flammable tobacco - pyrethrum spray form F-13 | Tobacco insecticide | Carmel Chem. Corp.<br>Westfield, IL | 60% |
| Pybutox - aerosol - F-201 D | Insecticide/miticide | Gabriel Chemical<br>Paterson, NJ | - |
| Gabriel DD-VP-90% conc. | Insecticide/miticide | Gabriel Chemical<br>Paterson, NJ | 10% |
| Moorehead 5% DD-VP spray | | Moorehead Ind., Inc.<br>Hopkinton, MA | 20% |

# APPENDIX E

# PHYSICAL PROPERTIES
# OF
# METHYL CHLOROFORM

| | Methyl chloroform |
|---|---|
| Chemical Abstracts Service registry number | 71-55-6 |
| Molecular formula | $C_2H_3Cl_3$ |
| Structure |  $\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{C}}{-}\overset{H}{\underset{H}{C}}{-}H}$ |
| Molecular weight | 133.42 |
| Composition (% by wt) | C 18.00%<br>H 2.27%<br>Cl 79.72% |
| Boiling point, °C | 74 |
| Freezing point, °C | -37 |
| Flash point | None |
| Fire point | None |
| Vapor density | 4.55 |
| Specific gravity | 1.320 |
| Density, lb/gal | 10.99 |
| Specific heat, Btu/(lb)(°F) | 0.25 |
| Heat of vaporization, Btu/lb | 102 |
| Viscosity, cP at 25°C | 0.79 |

# PHYSICAL PROPERTIES OF METHYL CHLOROFORM INFLUENCING EVAPORATIVE LOSSES

| | |
|---|---|
| Solubility in water (ppm)a | 1,300 |
| Vapor Pressure no Hq(25°)a | 123 |
| Partition Coefficient b | 0.68 |
| Evaporation half-life, min c | 20±3 |

a - Kirk-Otmer Encyclopedia of Chemical Technology, 2nd edition, Interscience Publishers, N.Y.

b - c air/c water

c - Dilling, et.al. 1975.
Calculated at room temperature, with constant mixing.

# APPENDIX F

## BREATHING AND WORKING LOSSES

Breathing and working loss rates calculated in the following section for vented fixed roof tanks are based on equations found in AP-42 (EPA, 1977c) and assumptions used by Hydroscience (Hydroscience, 1979). These assumptions are presented in Table F-1.

The breathing loss equation is:

$$BL = 2.21 \times 10^{-4} M \left[ \frac{P}{14.7-P} \right]^{0.68} D^{1.73} H^{0.51} T^{0.50} C$$

BL = Fixed roof breathing loss (lb/day)*

M = Molecular weight of vapor in storage tank (lb/lb mole)

P = True vapor pressure at bulk liquid conditions (psia)

D = Tank diameter (ft)

H = Average vapor space height

T = Average ambient temperature cahnge from day to night (°F)

C = Adjustment factor for small diameter tanks (dimensionless)

The working loss equation is:

$$WL = 2.40 \times 10^{-2} MPN$$

WL = Fixed roof working loss (lb/$10^3$ gal throughput)

M = Molecular weight of vapor in storage tank (lb/lb mole)

---

* This loss is neglected if non-vented tanks are employed.

Table F-1 Assumptions Used in Breathing and Working Loss Rate Calculations

| Tank Type | Number of Tanks | Tank Volume ($M^3$) | Tank Height (ft) | Tank Diameter (ft) | Vapor at 27°C (psia) | Average Vapor Space Height (ft) | Temperature Change (±F) | Molecular Weight Vapor lb/lb mole | Turnover Factor | Small Diameter Adjustment Factor |
|---|---|---|---|---|---|---|---|---|---|---|
| Vinyl Chloride Process - Refined Product Tank | 4 | 598 | 30 | 30 | 2.6 | 15 | 20 | 133 | 0.9 | 1 |
| Vinyl Chloride Process - Crude Product Tank | 2 | 98 | 16 | 16 | 2.6 | 8 | 20 | 133 | 1 | .8 |
| Ethane Process Refined Product Tank | 4 | 174 | 20 | 20 | 2.6 | 10 | 20 | 133 | 1 | .9 |
| Ethane Process Crude Product Tank | 2 | 29 | 11 | 11 | 2.6 | 5.5 | 20 | 133 | 1 | .55 |

Source: Hydroscience, 1979; EPA, 1977c.

P = True vapor pressure at bulk liquid conditions (psia)

N = Turnover factor (dimensionless)

1) Total loss rate for vinyl chloride (VC) process for refined product storage (based on 136,000 kkg/year of refined product)

a) Breathing Loss for on tank:

$$BL = 2.21 \times 10^{-4}(133)\left(\frac{2.6}{14.7-2.6}\right)^{0.68}(30)^{1.73}(15)^{0.51}(20)^{.50}(1)$$

$= 64.3$ lbs/day

$= 29.2$ kg/day

For the process on an annual basis:

Total Breathing Loss = 0.31 kg/kkg

b) Working Loss:

$WL = 2.40 \times 10^{-2}\ (133)\ (2.6)\ (.9)$

$= 7.4\ lb/10^3$ gal.

$= .88$ kg/kkg

Total Emission Rate = .31 + .88 = 1.19 kg/kkg

2) Total loss rate for VC process for crude product storage (based on 136,000 kkg/year of refined product and 6,625 kkg of crude product throughout)

a) Breathing Loss for one tank:

$$BL = 2.21 \times 10^{-4} (133)\left(\frac{2.6}{14.7-2.6}\right)^{0.68}(10)^{1.73}(8)^{0.51}(20)^{.50}(.8)$$
$= 12.6$ lbs/day
$= 5.8$ kg/day

For the process of an annual basis:

Total Breathing Loss = .03 kg/kkg

b) Working Loss

$$WL = 2.40 \times 10^{-2} (133)\ (2.6)\ (1)$$
$= 8.3$ lb/$10^3$ gal
$=$ .98 kg/kkg oc crude product throughput

For the process on an annual basis:

Total Working Loss = .98 x (6,625 kkg of crude throughput)/
(136,000 kkg of production)
= .05 kg/kkg of production

Total Emission Rate - .03 + .05 = .08 kg/kkg

3) Total loss rate for the Ethane process for refined product storage (based on 29,500 kkg/year of refined product)

a) Breathing Loss (for fixed roof tanks only) for one tank:

$$BL = 2.21 \times 10^{-4} (133)\left(\frac{2.6}{14.7-2.6}\right)^{0.68} (20)^{1.73}(10)^{.51}(20)^{.50}(.9)$$
$= 23.3$ lbs/day
$= 10.6$ kg/day

For the process on an annual basis:

Total Breathing Loss = .52 kg/kkg

b) Working Loss

$$WL = 2.40 \times 10^{-2}(133)(2.6)(1)$$
$$= 8.3\ \text{lbs}/10^3\ \text{gal}$$
$$= .98\ \text{kg/kkg}$$

Total Emission Rate = .52 - .98 = 1.50 kg/kkg

4) Total loss rate for the Ethane process for crude product storage (based on 29,500 kkg/year of refined product and 1,660 kkg of crude product throughput)

a) Breathing Loss (for fixed roof tanks only) for one tank:

$$BL = 2.21 \times 10^{-4}\ (133)\ \left(\frac{2.6}{14.7-2.6}\right)^{0.68}(11)^{1.73}(5.5)^{0.51}\ (20)^{.50}\ (.55)$$
$$= 3.7\ \text{lbs/day}$$
$$= 1.7\ \text{kg/kkg}$$

For the process on an annual basis:

Total Breathing Loss = .04 kg/kkg

b) Working Loss

$$WL = 2.40 \times 10^{-2}\ (133)\ (2.6)\ (1)$$
$$= 8.3\ \text{lbs}/10^3\ \text{gal}$$
$$= .98\ \text{kg/kkg of crude product throughput}$$

For the process on an annual basis:

Total Working Loss = .98 x (1,660 kkg of crude throughput)/
(29,550 kkg of production)
= .06 kg/kkg

Total Emission Rate = .04 + .06 = .10 kg/kkg